CODING FORMS FOR SRC INDEXING

Microfiche No.	
	OTS0557274

New Doc ID		Old Doc ID	
			86940000864

Date Produced		Date Received		TSCA Section	
02/10/94		05/27/94		8D	

Submitting Organization	
INTL ISOCYANATE INST INC	

Contractor	
CHEM INSPECTION & TESTING INST	

Document Title	
FINAL REPORT: STUDY ON THE FATE OF POLYMERIC METHANE DIISOCYANATE (MDI) IN WATER WITH COVER LETTER DATED 05/24/94	

Chemical Category	
POLYMERIC METHANE DIISOCYANATE (9016-87-9)	

Microfiche No. (7) *		1	No. of Pages		2
Doc I.D.		3	Old Doc I.D.	8694 000 0864	4
Case No.(s)					5

Case No.(s) _____ 11

| Date Produced (6) | | 6 | Date Rec'd (6) | | 7 | C s. Code * | | 8 |

Check One: ☐ Publication   ☐ Internally Generated   ☐ Externally Generated

Pub/Journal Name		9
		9
Author(s)		10
Organ. Name		11
Dept/Div		12
P.O. Box	13	Street No./Name	14
City	15	State	16	Zip	17	Country	18
MID No. (7)	19	D & B No. (11)	20
Contractor		21
Doc Type		22

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| Doc Title | | 23 |

| Chemical Name (300 per name) | 25 | CAS No. (*3) | 24 |

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May 24, 1994

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Dear Sir or Madam:

As required by 40 CFR 716, as amended, we herewith submit a copy of the following recently completed health and safety study.

Fate of Polymeric MDI in Water, Part II, Project FE-E-74

Chemical Name	CAS Number
MDI monomer 2,4' isomer	05873-54-1
MDI monomer 4,4' isomer	00101-68-8
MDI monomer 2,2' isomer	02563-05-2
MDI isomer Mixture	26447-40-5
Polymeric MDI	09016-87-9
4,4' MDA	00101-77-9

The International Isocyanate Institute (III) reference number 11122 has been marked at the top of the title page of this report. Please refer to this III identification number in any communication regarding this study. **The enclosed report does not contain any Confidential Business Information.**

The study is sponsored by the International Isocyanate Institute on behalf of the following:

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Final Report
Study on the fate of polymeric MDI in water

FE-E-74   Part II

February 10, 1994

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Kurume Research Laboratories
Chemical Biotesting Center
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Content

Abstract

The fate of polymeric MDI in water was studied under two conditions, vigorous stirring and static conditions, which simulate two scenarios of accidental spill of polymeric MDI into aquatic environment. The kinetics of the disappearance of polymeric MDI and the production of water-soluble and water-insoluble reaction products were examined for each experiment and the following results were obtained:

(1) Vigorous stirring experiment

The experiment was carried out with varying nominal concentration of polymeric MDI, temperature, salinity and agitation method of test solution.

- Kinetics of disappearance of polymeric MDI

Polymeric MDI disappeared linearly with time under all conditions, indicating that the disappearance of polymeric MDI is expressed by zero-order kinetic model. The disappearance rate data for each of five or six constituents of polymeric MDI, whose number of aromatic ring ranged from two to four, were fitted to zero-order kinetic model and the zero-order rate constant and the half-life time of the disappearance were determined by least squares method as a function of nominal concentration of polymeric MDI and temperature, salinity and agitation method of the test solution. The rate constant increased approximately linearly with nominal concentration of polymeric MDI for all constituents and it was smaller with the constituent having more number of aromatic ring, but half-life time was independent on the nominal concentration and the kind of constituent. Gentle agitation, high salinity and low temperature of the test solution lowered the disappearance rate. Especially the temperature of the test solution significantly affected the rate: the half-

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life time at 25°C was less than one quarter of the value at 12°C.

- Production of water-soluble reaction products

4,4'-MDA increased gradually with time and reached to nearly constant concentration after 16th-hour, at which over 60% of initial polymeric MDI remained intact. Final amount of 4,4'-MDA produced increased slightly with nominal concentration of polymeric MDI and consequently the proportion of polymeric MDI transformed to 4,4'-MDA against total amount of polymeric MDI added decreased rapidly with the nominal concentration. The proportion was less than 0.5% at the nominal concentration of 400mg/l or above (Figure 20). The water-soluble reaction products other than 4,4'-MDA were not observed with both UV spectrum and HPLC.

- Water-insoluble reaction products

Water-insoluble reaction products was not completely soluble in toluene and DMF. The fraction of the reaction products insoluble in both solvents increased with test duration. Only 6.6% of final water-insoluble reaction products were dissolved in DMF containing 10 mM of LiCl (Table 4).

Consequently, it was concluded that over 92.9% of polymeric MDI was finally transformed in vigorous stirring experiment to the polyurea insoluble in water and usual organic solvent.

(2) Static experiment

The kinetics of the disappearance of polymeric MDI and the productions of water-soluble and water-insoluble reaction products were measured under three interfacial area between polymeric MDI and water phases (5.72, 13.2 and 18.1 cm^2).

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- Kinetics of disappearance of polymeric MDI

Polymeric MDI also disappeared by zero-order kinetics except the experiment of the interfacial area of 5.72 cm^2, in which polymeric MDI disappeared by zero-order kinetics until 10 days, but the disappearance rate largely slowed down thereafter. The zero-order rate constant increased and the half-life time decreased with the interfacial area between polymeric MDI and water phases.

- Water-soluble reaction products

The production of 4,4'-MDA gradually increased and reached to the constant value with the disappearance of polymeric MDI. The final amount of 4,4'-MDA produced was about 0.6mg/l (Figure 30), which corresponded to less than 0.005% of the initial amount of polymeric MDI added, and it was independent on the interfacial area. The water-soluble reaction products other than 4,4'-MDA were observed with UV spectrum and HPLC, but the structure was not identified because of small amount.

- Water-insoluble reaction products

The solubility of the water-insoluble reaction products to toluene and DMF lowered with time. After 4 weeks in the experiments of 18.1 cm^2 interfacial area, 99.3% of the products were insoluble to both water and usual organic solvents and only 0.7% of it was soluble to DMF containing 10mM of LiCl (Table 4).

Consequently, it is concluded that polymeric MDI was transformed to water-soluble substance at less than 0.04% of polymeric MDI added and the remaining polymeric MDI was transformed to the substance insoluble to toluene. Only 0.7% of the tolune-insoluble reaction products was dissolved in DMF containing LiCl and 99.7% of it is insoluble in both water and usual organic solvent including DMF-LiCl.

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Introduction

Since isocyanate compound easily react with water to produce the corresponding amine, which reacts with other isocyanate compounds and is transformed to urea compound, it is indispensable in assessment of the ecotoxicologycal effect of the isocyanate compound to elucidate the fate in water.

In FE-E-63 project, we studied the fate of TDI in water under two conditions, vigorous stirring and static conditions, which simulate two scenarios of accidental spill of TDI into aquatic environment in order to elucidate the fate of TDI in aquatic environment and to explore the origin component for the toxicity to aquatic organisms in successive ecotoxicity test of TDI in FE-66 project.

Polymeric MDI is another raw material of polyurethane that is produced in large scale and it is important to clarify the fate in water for assessing the effect of polymeric MDI on the aquatic environment. In part I of FE-74 project, the analytical method of polymeric MDI and the agitation method suitable for vigorous stirring experiment of polymeric MDI were examined using monomeric polymeric MDI as a test substance. On the basis of these results, in this study (FE-74 Part II) the fate of polymeric MDI in water was investigated prior to the toxicity test.

The experiment was conducted under two conditions, vigorous stirring and static conditions, in a similar procedure as TDI. The time courses of the disappearance of polymeric MDI and the production of water-soluble reaction products including 4,4'-MDA and water-insoluble ones were measured with varying the nominal concentration of polymeric MDI and the temperature, the salinity and the agitation method of the test solution for the vigorous stirring experiment and with varying the interfacial area between water and polymeric MDI phases for static experiment. The data were interpreted from the kinetic point of view.

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2. Materials and methods

2.1 Materials

(1) Test substance

Millionate MR-200 of Nippon Polyurethane Industry Co., Ltd. was used for a test substance. The properties of this substance are as follows:

Content of NCO	31.1 wt%
Acidity as HCL	0.01 wt%
Viscosity	172 cP/25°C
Specific gravity	1.236

The composition of the test substance was determined as follows: One ml of 5 wt% solution of the test substance in toluene was mixed with equal volume of 6 wt% solution of dibutylamine (DBA) in toluene and was allowed to stand for several minutes. The solution was diluted with acetonitril and analyzed with HPLC under the following condition:

Apparatus	:Shimadzu LC-6A
Column	:L-column ODS (4.6 mmID x 150 cmL)
Eluent	:Acetonitril
Flow rate	:1 ml/min
Detection	:250 nm
Range	:0.01 AUFS
Inj. volume	:10 ul

Typical chromatogram is shown in Figure 1. More than ten peaks were separated, in which six peaks with enough peak areas were selected for the study of the disappearance kinetics of polymeric MDI. The content of each constituent in the substance was determined from the ratio of the peak area. The result is shown in Table 1.
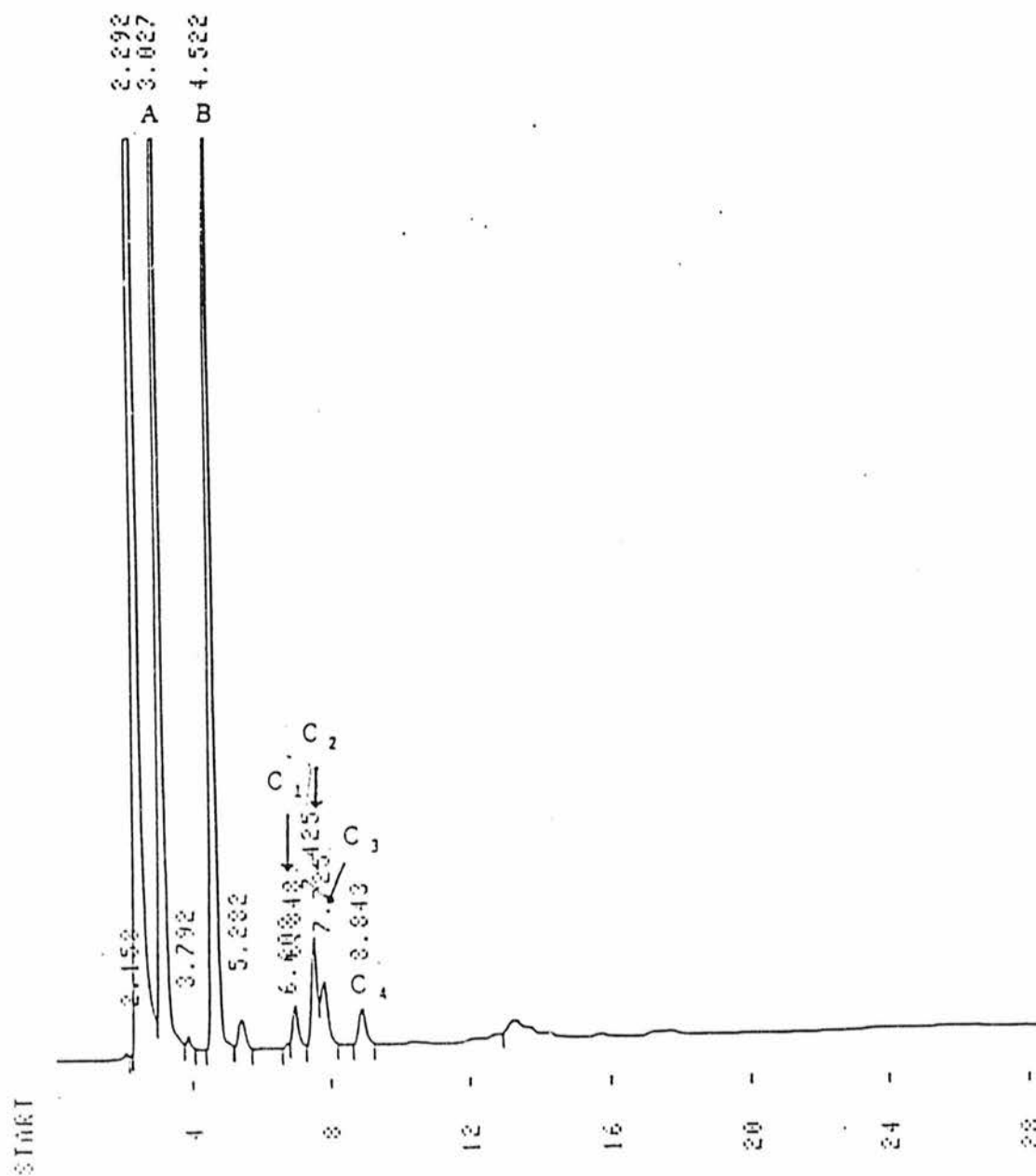
Figure 1. Typical chromatogram of dibutylamine derivative of polymeric MDI used in this study.

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Table 1 Composition of polymeric MDI used in this study

Peak	Number of aromatic ring in constituent	Percent peak area (%)
A	2	54.5
B	3	32.4
C1	4	1.97
C2	4	3.46
C3	4	2.62
C4	4	1.37
-	5	3.2
..	6	0.5
	total	100

(2) Water and artificial sea water

Distilled water purified by ion-exchange (Purified water frim Takasugi Seiyaku Co., Ltd..) was used in all experiments. The artificial sea water was prepared by dissolved the following inorganic salts in water.

Constituents	Concentration (mg/l)
NaF	3
$SrCl_2 6H_2O$	20
H_3BO_3	30
KBr	100
KCl	00
$CaCl_2 2H_2O$	1470
Na_2SO_4	4000

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$MgCl_2 6H_2O$	10780
NaCl	23500
$Na_2SiO_3 9H_2O$	90
Na_4EDTA	1
$NaHCO_3$	200

(3) Reagents

All the reagents used in this study were of guaranteed reagent grade and used as received.

2.2 Methods

2.2.1 Vigorous stirring experiment

(1) Disappearance of polymeric MDI and production of 4,4'-MDA and other reaction products

20mg, 50mg or 500mg of polymeric MDI was applied to inner side wall of 100 ml Erlenmeyer flask and 50 ml of water or artificial sea water was poured into it. The test substance was applied to inner wall of the flask in order to prevent adhesion of MDI to the stirrer bar during the test, which stops stirring of the test solution. The solution was stirred at 1500 + 500 rpm with magnetic stirrer and Teflon stirrer bar (8mm diameter, 40mm length) or was shaken at 200rpm with a rotary shaker (TAITEC Double Shaker NR-3) at 25°C or 12°C. At appropriate intervals, the residual amount of polymeric MDI, the concentrations of dissolved organic carbon (DOC), 4,4'-MDA and the toluene-insoluble reaction products were determined as follows:
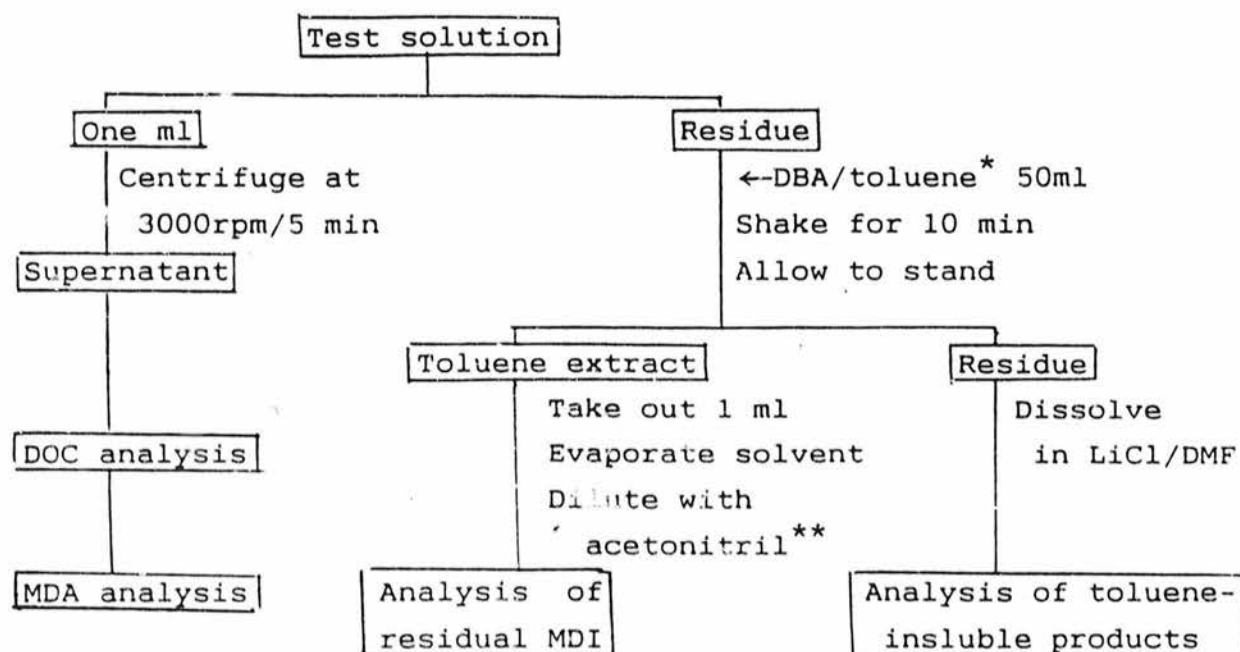
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```
                          ┌──────────────┐
                          │Test solution │
                          └──────┬───────┘
              ┌──────────────────┴──────────────────────┐
         ┌─────────┐                              ┌──────────┐
         │ One ml  │                              │ Residue  │
         └─────────┘                              └──────────┘
           Centrifuge at                      ←-DBA/toluene* 50ml
           3000rpm/5 min                        Shake for 10 min
         ┌─────────────┐                         Allow to stand
         │ Supernatant │
         └─────────────┘
                              ┌──────────────────┴──────────────────┐
                        ┌─────────────────┐                  ┌──────────┐
                        │ Toluene extract │                  │ Residue  │
         ┌──────────────┐└─────────────────┘                 └──────────┘
         │ DOC analysis │    Take out 1 ml                     Dissolve
         └──────────────┘    Evaporate solvent                  in LiCl/DMF
                             Dilute with
         ┌───────────────┐     acetonitril**
         │ MDA analysis  │  ┌─────────────────┐         ┌─────────────────────┐
         └───────────────┘  │ Analysis   of   │         │ Analysis of toluene-│
                            │ residual MDI    │         │ insluble products   │
                            └─────────────────┘         └─────────────────────┘
```

Figure 2. Flow scheme of the analyses of residual polymeric MDI
and the reaction products in vigorous stirring experiment.

* The concentration of dibutylamine: 480mg/l. 1200mg/l and 1.2g/l for the nominal concen-
tration of polymeric MDI of 400mg/l. 1000mg/l and 10000mg/l. respectively.

** Final volume: 4ml. 10ml and 100ml for the nominal concentration of polymeric MDI of
400mg/l. 1000mg/l and 10000mg/l. respectively.

    DOC was measured with TOC analyzer and polymeric MDI and
4,4'-MDA were determined with HPLC under following conditions:

Analytical conditions

- Analysis of DOC
    Apparatus   : Shimadzu Total organic carbon analyzer
                      TOC-500
    Furnace temp.: 680°C

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```
Flow rate      : 150ml/1
Inj. volume    : 10 ul
Sensitivity    : Range 3
```

- Analysis of polymeric MDI and 4,4'-MDA
```
Apparatus   : Shimadzu LC-6A
Column      : L-column ODS (4.6 mmID x 150 cmL)
Eluent      : Acetonitril for polymeric MDI
              Acetonitril/water=3/2(v/v) for 4,4'-MDA
Flow rate   : 1 ml/1
Detection   : 250 nm
Range       : 0.01 AUFS
Inj. volume : 10 ul
```

- Analysis of Toluene-insoluble reaction products
```
Apparatus   : Shimadzu LC-4A
Column      : Shodex AD 80M (8 mmID x 300 cmL)
Eluent      : DMF containing 10 mM LiCl
Flow rate   : 1 ml/1
Detection   : 292 nm
Range       : 0.08 AUFS
Inj. volume : 10 ul
Temperature : 40°C
```

The recovery test of polymeric MDI was carried out in dupli-
cates for 50 mg of polymeric MDI. The average recoveries for six
peaks were nearly 100% except C1 peak (Table 2) and therefore the
recoveries did not be corrected in calculating the residual
amounts of polymeric MDI.

In order to examine the disappearance of polymeric MDI and
the production of 4,4'-MDA at lower nominal concentration of
polymeric MDI, 100ul and 500ul of 1% solution of polymeric MDI in
DMSO was added to 50ml of water with stirring and the time

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course of the disappearance of polymeric MDI and the production
of 4,4'-MDA were measured by the same method.

Table 2. The recoveries for six peaks of polymeric MDI
from water in vigorous stirring experiment

Peak	Recoveries(%)		
	1	2	Average
A	100.8	99.3	100.1
B	100.6	100.4	100.5
C1	93.4	93.0	93.2
C2	100.9	103.3	102.1
C3	100.8	98.8	99.8
C4	101.9	103.6	102.8

(2) Analysis of final water-soluble reaction products

At the end of the experiment in which 50mg of polymeric MDI
was stirred in 50ml of water at 1500rpm with magnetic stirrer at
25°C, the aliquot of the solution was centrifuged at 3000rpm and
the uv spectrum of the supernatant was measured in order to
detect the water-soluble reaction products other than 4,4'-MDA.
Also the solution was analyzed with ODS column under varied
eluents to survey the water-soluble reaction products.

(3) Analysis of final water-insoluble reaction products

The properties of final water-insoluble reaction products
were examined as follows: 50mg of polymeric MDI was put in each
of ten Erlenmeyer flasks, which were divided in two groups con-

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sisting of five flasks, and 50ml of water was poured into it and stirred for 2 weeks. 50ml of toluene was added to each flask and shaken for 10 minutes. After the solution was allowed to stand to separate water and toluene layers, the solution was filtered with a filter paper. All five solutions belonging to the same group were filtered with the same filter paper. The residue on the filter paper was air-dried at 50°C for 2 hours, dried in desiccator overnight and was ground. 0.1g of it was added to 10ml of DMF containing 10mM of LiCl and was shaken to extract the substance soluble in the solvent. The extract was centrifuged at 3000rpm for 10 minutes and was analyzed with HPLC under the same condition as 2.2.1 (1). The amount of the substance soluble in the solvent was determined on the basis of the peak area of the standard solution of DBA derivative of polymeric MDI.

(4) Analysis of the disappearance kinetics of polymeric MDI

The percent residue for each constituents of polymeric MDI were fitted to the following zero-order reaction kinetic equation and the slope were determined by the linear least squares method;

$$R = R_0 - S * t \qquad\qquad \text{equation 1}$$

where R = percent residue, R_0 = constant, S = slope and t = time. The rate constant, k, and half-life time, $t_{1/2}$, for each constituent was calculated from the following equation;

$$k = S * (\text{amount of each constituent added})/100$$

<div align="right">equation 2</div>

and

$$t_{1/2} = R_0/(2 * S) \qquad\qquad \text{equation 3}$$

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2.2.2 Static experiment

(1) Disappearance of polymeric MDI and production of 4,4'-MDA and other reaction products

5g of polymeric MDI in 10ml, 50ml or 100ml beaker (27mmφ x 50mm height, 41mmφ x 60mm height and 48mmφ x 67mm height, respectively) were placed on the bottom of 300ml tall beaker (60mmφ x 130mm height) containing 300ml of water and were allowed to stand in water bath thermostated at 25°C. At appropriate intervals, the inner beaker was taken out from the tall beaker and the concentrations of DOC and 4,4'-MDA in water, the amount of the residual polymeric MDI and toluene-insoluble reaction products were analyzed as follows;

```
                        ┌─────────────┐
                        │Test solution│
                        └─────────────┘
                          │take out inner beaker containing MDI
          ┌────────────────┴──────────────────────────┐
    ┌───────────┐                                ┌──────────┐
    │Water phase│                                │MDI phase │
    └───────────┘                                └──────────┘
 ┌──────┐                      ┌────────┐              │
 │One ml├──────────────────────│Residue │              │
 └──────┘                      └────────┘              │
     │Centrifuge at              │Filtrate             │
     │3000rpm/10min   Filtrate   │Residue              │
┌───────────┐              ┌───────────────────────────────┐
│Supernatant│              │MDI + suspended substance      │
└───────────┘              └───────────────────────────────┘
     │                          │<─DBA 30g/1 toluene 200ml
     │                          │React
     │                          │Allow to stand
┌─────────────┐       ┌────────────────┐        ┌─────────┐
│DOC analysis │       │Toluene extract │        │Residue  │
└─────────────┘       └────────────────┘        └─────────┘
     │                  │Dilute to 250ml          │Dissolve in
     │                  │withdraw the aliquot      │10ml LiCl/DMF
┌─────────────┐         │Dilute by acetonitril     │
│MDA analysis │    ┌────────────┐           ┌──────────────────┐
└─────────────┘    │Analysis of │           │Analysis of toluene-│
                   │residual MDI│           │insoluble products  │
                   └────────────┘           └──────────────────┘
```

Figure 3.   Flow scheme of the analyses of residual polymeric MDI and the reaction products in static experiment.

The interfacial area between water and polymeric MDI phases were 5.72cm^2, 13.2cm^2 and 18.1cm^2 for the experiments using 10ml, 50ml and 100ml beakers, respectively.

The analytical conditions for DOC, 4,4'-MDA, polymeric MDI and toluene-insoluble reaction products were the same as vigorous stirring experiment. Recoveries were nearly 100% for all constituents of polymeric MDI (Table 3) and was not taken into account in calculation of residual amount of polymeric MDI.

Table 3. The recoveries for main six peaks of polymeric MDI from water in static experiment

Peak	Recoveries(%)
A	101.8
B	98.9
C1	98.3
C2	97.5
C3	102.0
C4	103.2

(2) Analysis of final water-soluble reaction products

At the end of the experiment of 18.1 cm^2 interfacial area (at 14th-day of the test), about 10 ml of the water pahse was withdrawn, centrifuged at 3000 rpm and its uv spectrum was measured in order to explore the water-soluble reaction products other than 4,4'-MDA. The solution also was analyzed with HPLC under varied eluents.

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(3) Analysis of final water-insoluble reaction products

The properties of final water-insoluble reaction products was examined as follows: 5g of polymeric MDI was put in each of two 100ml of beakers and submerged in 300ml tall beaker containing 300ml of water and allowed to stand at 25°C for 4 weeks. The inner beaker containing polymeric MDI was taken out and the water was filtered to collect the suspended substance with filter paper. The residue on the filter paper was combined with polymeric MDI in the beaker and was added to 200ml of toluene. After being shaken for 10 minutes, the toluene was filtered with filter paper. The residue on the filter paper was air-dried at about 50°C for 2 hours, dried in desiccator overnight and was ground. 0.1g of it was added to 10ml of DMF containing 10mM of LiCl and was shaken to extract the substance soluble in this solvent. The extract was centrifuged at 3000rpm for 10 minutes and was analyzed with HPLC under the same condition as 2.2.1 (1). The amount of the substance soluble in the solvent was determined on the basis of the peak area of the standard solution of DBA derivative of polymeric MDI.

(4) Analysis of the disappearance kinetics of polymeric MDI

The percent residue of each constituent of polymeric MDI was analyzed by zero-order reaction kinetic model and the rate constant and half-life time for each constituent of polymeric MDI were determined by the same method as vigorous stirring experiment.

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3. Results

3.1 Vigorous stirring experiment

3.1.1 Kinetics of polymeric MDI disappearance

Polymeric MDI was applied on inner side wall of 100ml erlen-
meyer flask in order to prevent stopping of stirring during test
period by adhering polymeric MDI to the stirrer bar. Polymeric
MDI changed from dark brownish liquid to pale yellow solid with
time and the majority of polymeric MDI was taken off from the
wall.

Figure 4 shows the variation in chromatogram of DBA deriva-
tive of residual substance together with that of standard solu-
tion. All peaks of polymeric MDI diminished simultaneously with
time without changing the elution pattern. Several peaks of
transient intermediates were observed between the peaks A and B,
between the peaks B and C1, near the peak C4 and so on. The peak
near the peak C4 could not be separated completely from the peak
C4 and therefore the residual amount of the peak C4 could not be
determined in most experiments.

Figure 5 to 7 show time courses of percent residues of five
or six constituents of polymeric MDI under three nominal concen-
trations of polymeric MDI. The data were applied to two kinetic
models, zero-order and first-order kinetic models, but they were
more fitted to zero-order kinetic model than first-order one.
The straight lines in these figures show the regression curves
determined by least squares method for zero-order kinetic models.
Figure 8 shows the slope of the regression curve as a a function
of the kind of the constituent of polymeric MDI and the nominal
concentration of polymeric MDI. The slopes were little dependent
on the nominal concentration of polymeric MDI with all constitu-
ents.

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The zero-order rate constant and half-life time of the disappearance of each constituent of polymeric MDI was calculated from the slope by equations 2 and 3, respectively. Figure 9 and 10 show the variation in rate constant and half-life time with the nominal concentration of polymeric MDI and with the kind of the constituent of polymeric MDI, respectively. The rate constant increased in proportion to the nominal concentration of polymeric MDI and to the content of the constituent, while half-life time was independent on the kind of the constituent and the nominal concentration of polymeric MDI.

In order to examine the disappearance kinetics of polymeric MDI at lower level of polymeric MDI added, polymeric MDI was added to water with stirring in DMSO solution at the nominal concentration of 20mg/l and 100mg/l. More than 50% of initial polymeric MDI disappeared within 2 hours in both experiments (Figure 11).

The kinetics of the disappearance of polymeric MDI is thought to be affected by a wide variety of the conditions in natural environment. Among these conditions, the agitation method, temperature and salinity of test solution are important because the reactivity of polymeric MDI with water depends on these factors. Hence the experiments were conducted with varying in the temperature, the salinity and the agitation method of the test solution at the nominal concentration of 1000mg/l. Figure 12 to 14 show the residual curves for five constituents of polymeric MDI under three conditions varying in these parameters. All data were also fitted to zero-order kinetic model. Figure 15 shows the comparison of the variation in the rate constant and half-life time with the kind of the constituent for four experiments. The dependencies of both values on the kind of the constituent of polymeric MDI were nearly identical with four conditions. Figure 16 shows the comparison of rate constants and half-life times for five constituents under four conditions. The salinity of test

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solution affected little the disappearance kinetics, but gentle agitation and low temperature of the test solution lowered the disappearance rate of all constituents. Especially the effect of temperature was noticeable and the disappearance rate at 12°C was about one fourth of that at 25°C.
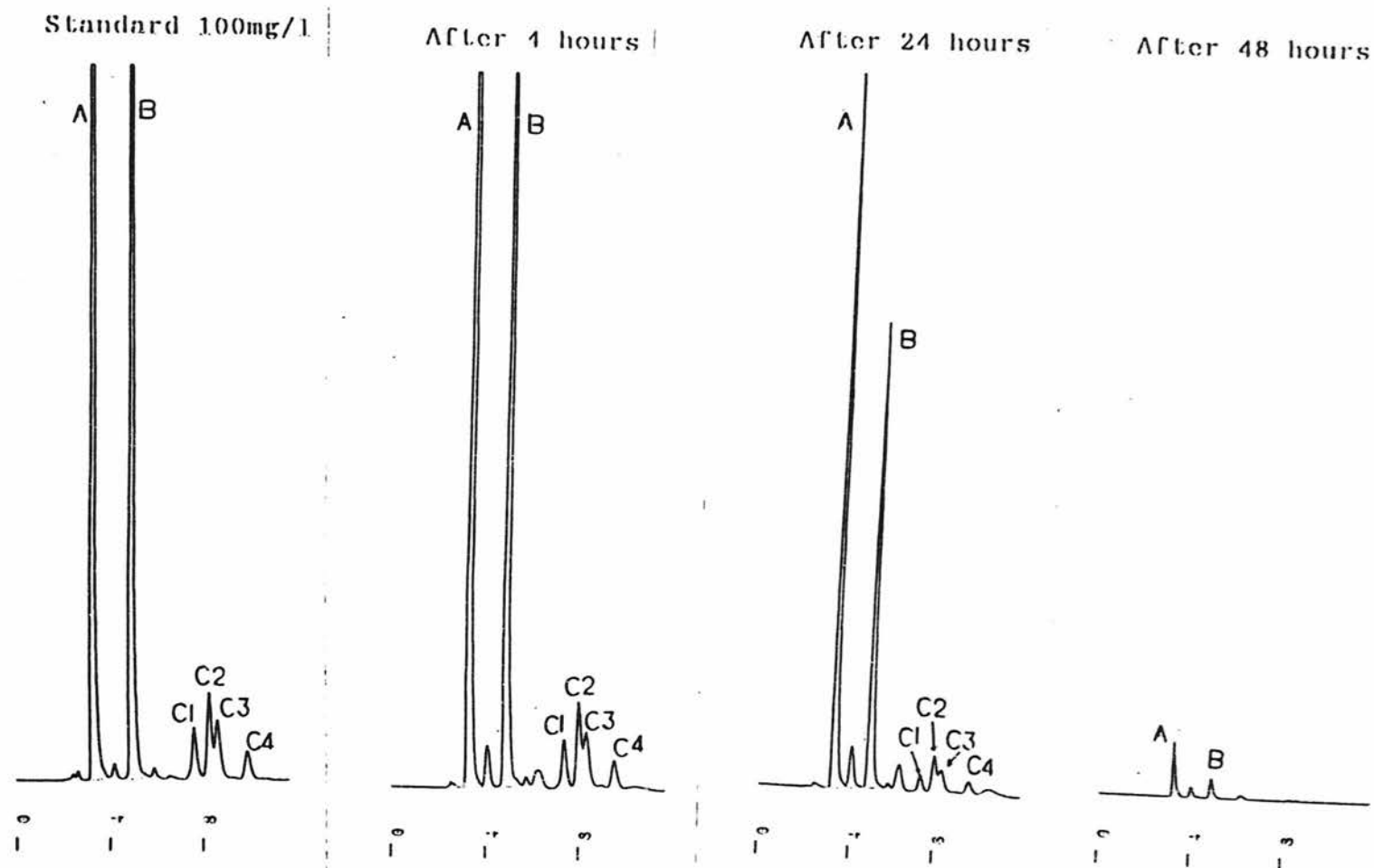
Figure 4. Variation i̇ omatogram of DBA derivative of residual substance in vigorous stirring experiment of polymeric MDI.
Test conditions: Nominal concentration; 1000mg/l, Stirring speed; 1500rpm, Temperature; 25°C.
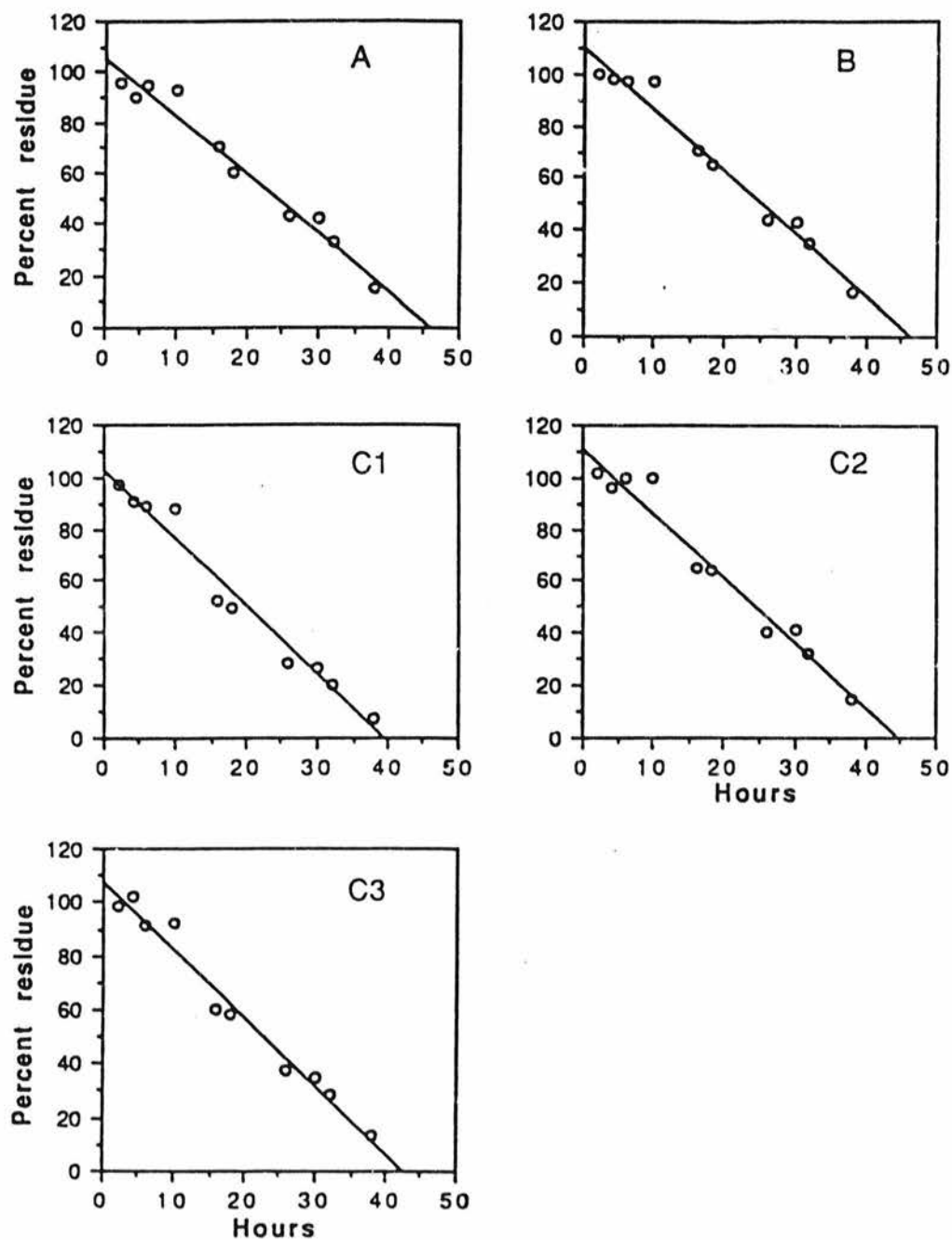
Figure 5. Residual curves of five constituents of polymeric MDI
in vigorous stirring experiment. The straight line indicate
linear regression curves to zero-order reaction equation.
Test conditions: Nominal concentration; 400mg/l, Stirring speed;
1500rpm, Temperature; 25°C.

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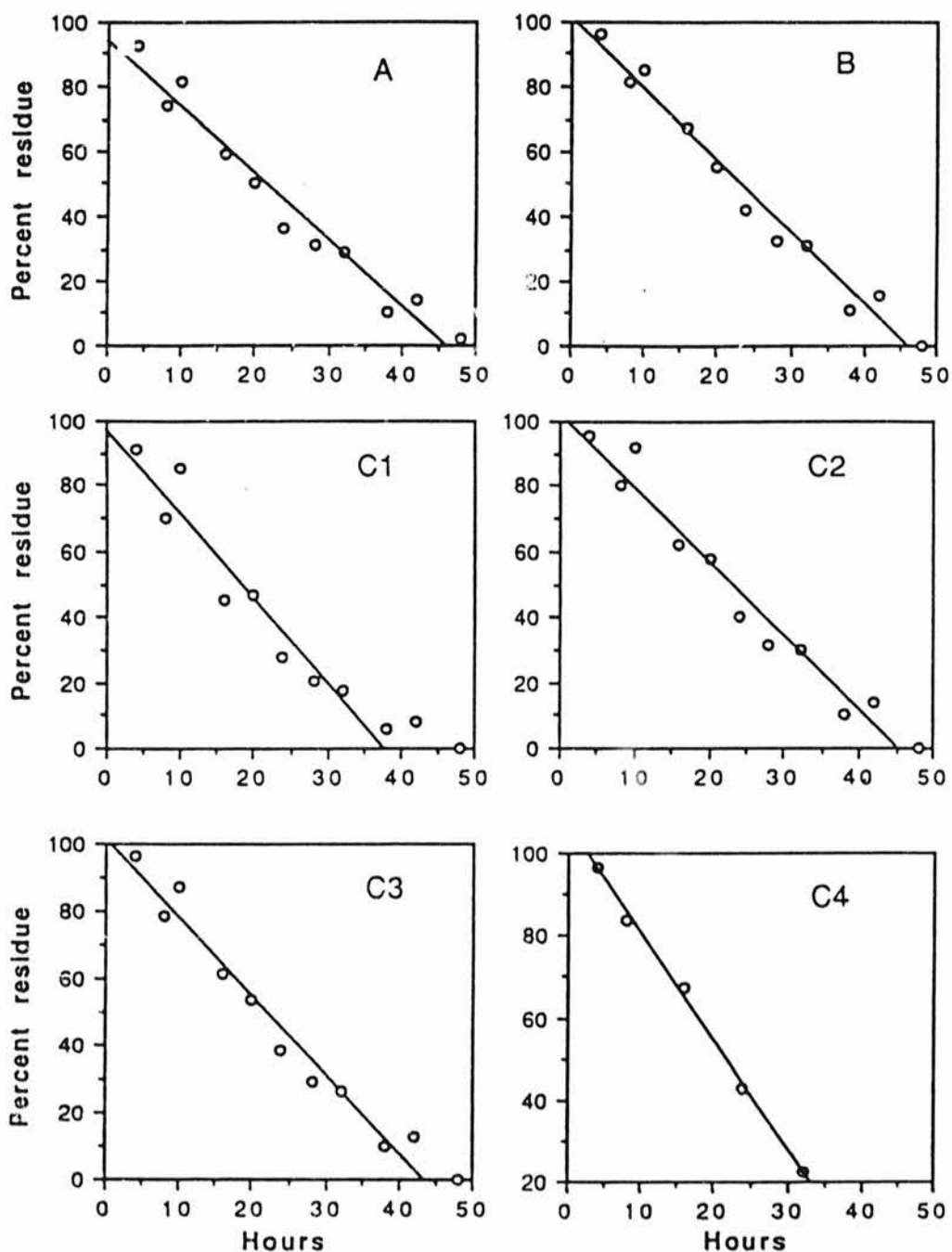
Figure 6. Residual curves of six constituents of polymeric MDI in vigorous stirring experiment. The straight line indicate linear regression curves to zero-order reaction equation.

Test conditions: Nominal concentration; 1000mg/l, Stirring speed; 1500rpm, Temperature; 25°C.

22
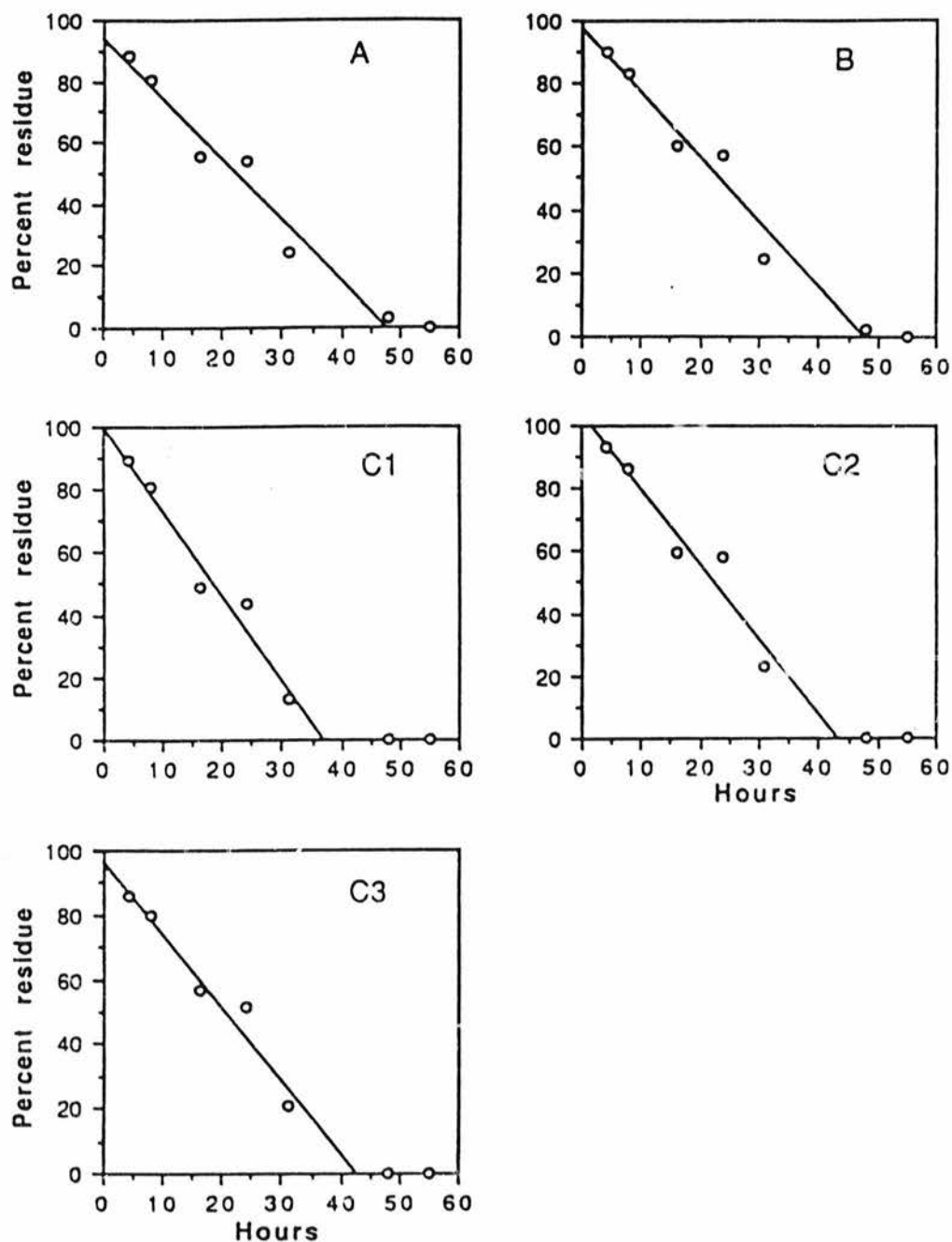
Figure 7. Residual curves of five constituents of polymeric MDI in vigorous stirring experiment. The straight line indicate linear regression curves to zero-order reaction equation.
Test conditions: Nominal concentration; 10000mg/l, Stirring speed; 1500rpm, Temperature; 25°C.

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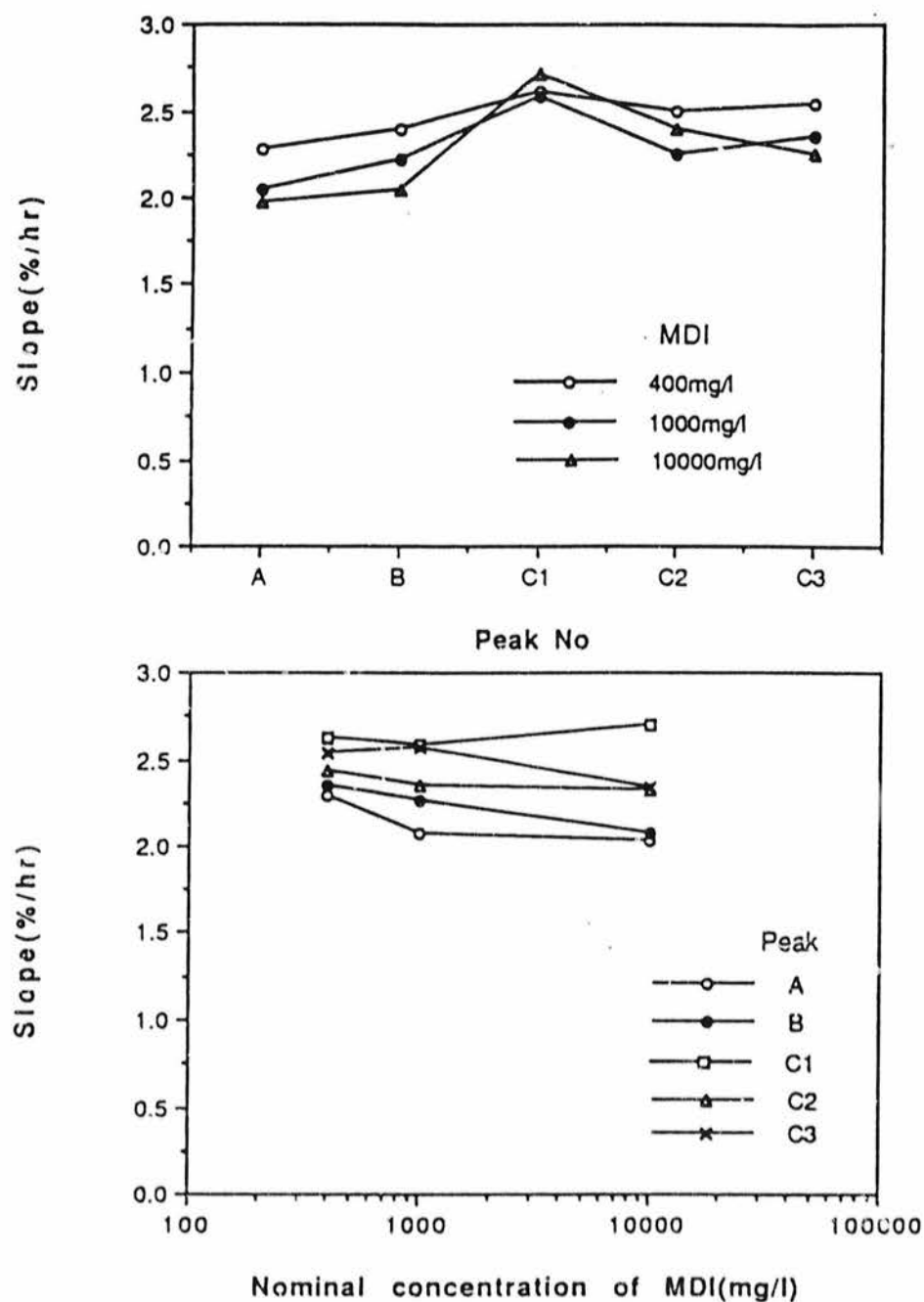
Figure 8. Comparison of slope of linear regression curve among five constituents of polymeric MDI (upper) and the relationship with the nominal concentration of polymeric MDI (bottom) in vigorous stirring experiment.

Test conditions: Stirring speed; 1500rpm, Temperature; 25°C.

24
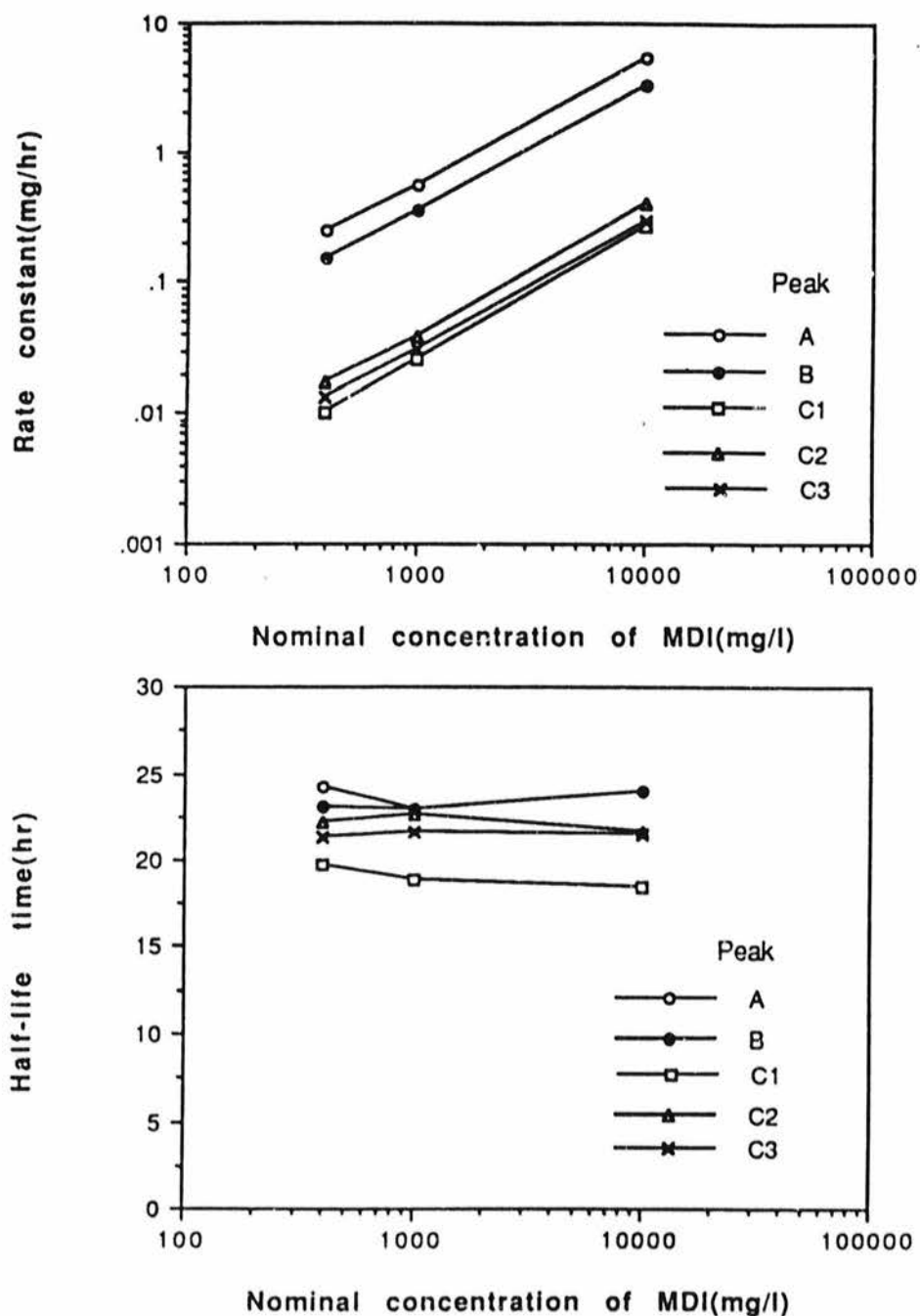
Figure 9. Relationships between zero-order disappearance rate constant (**upper**), half-life time (**bottom**) of five constituents of polymeric MDI and the nominal concentration in vigorous stirring experiment. Test conditions: Stirring speed; 1500rpm, Temperature; 25'C.

25
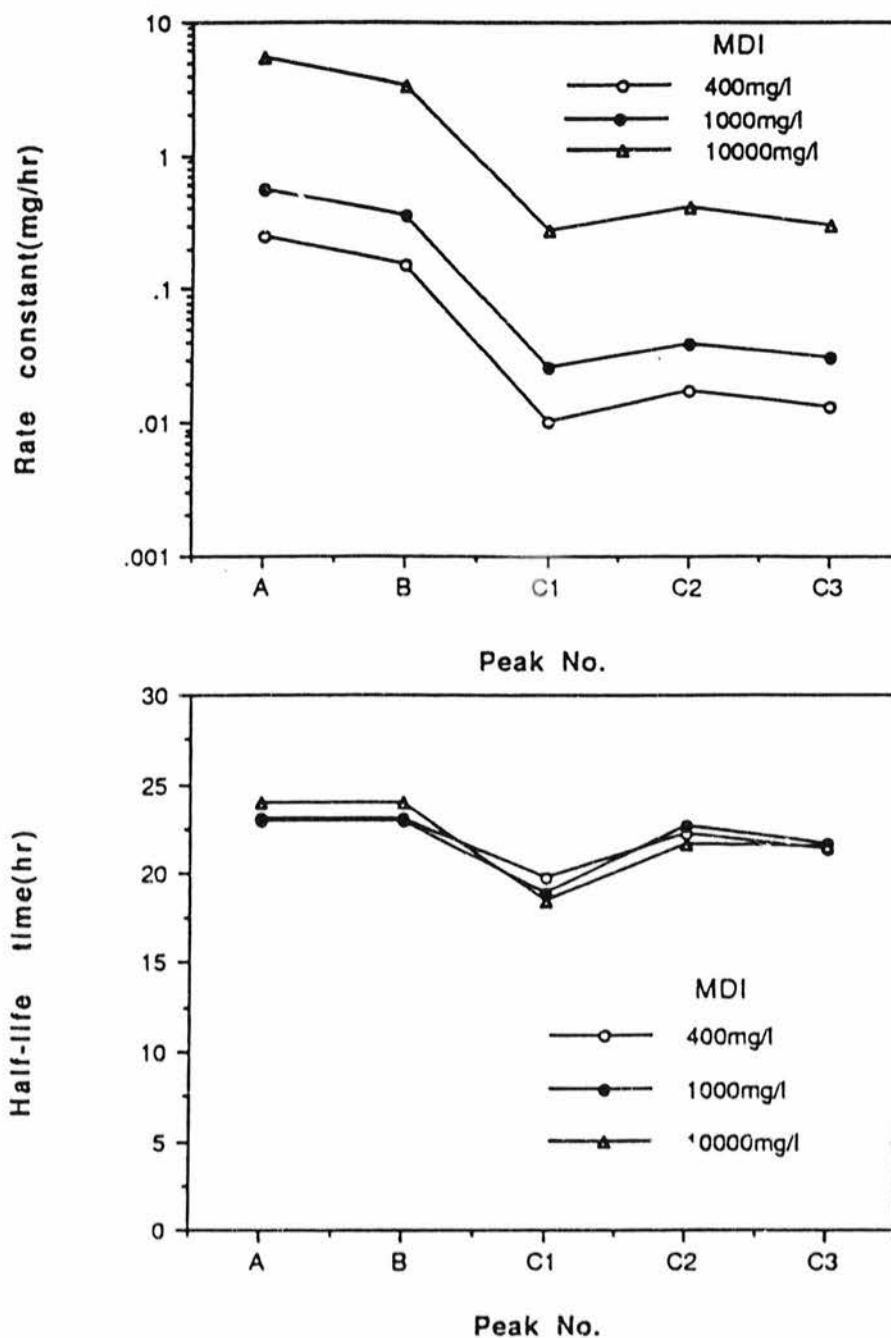
Figure 10. Comparisons of zero-order disappearance rate constant (upper), half-life time (bottom) among five constituents of polymeric MDI in vigorous stirring experiment.

Test conditions: Stirring speed; 1500rpm, Temperature; 25°C.

26
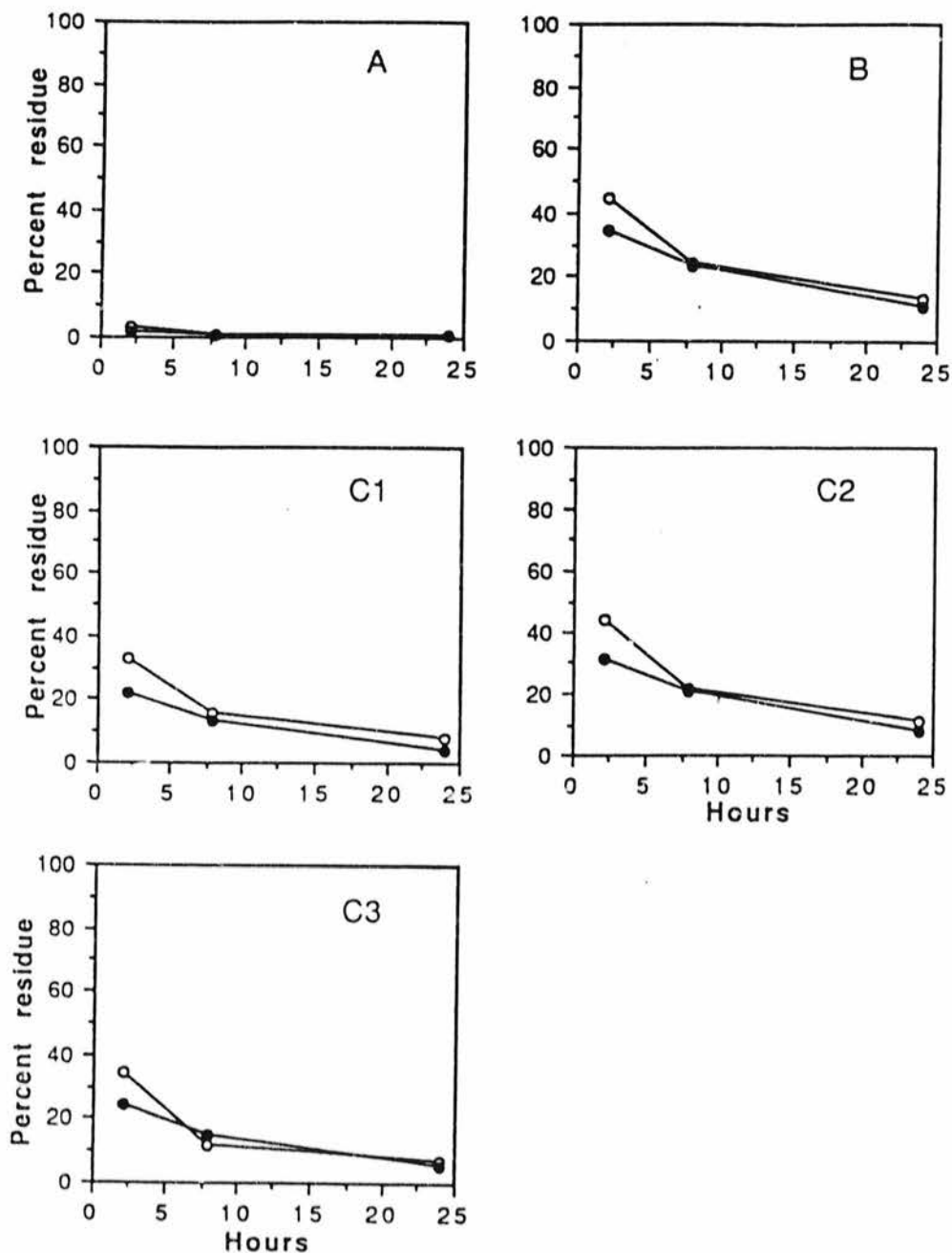
Figure 11. Residual curves of five constituents of polymeric MDI in vigorous stirring experiment. Polymeric MDI was added in DMSO solution. Test conditions: Nominal concentration; 20mg/l (●) and 100mg/l (o), Stirring speed; 1500rpm, Temperature; 25°C.

27
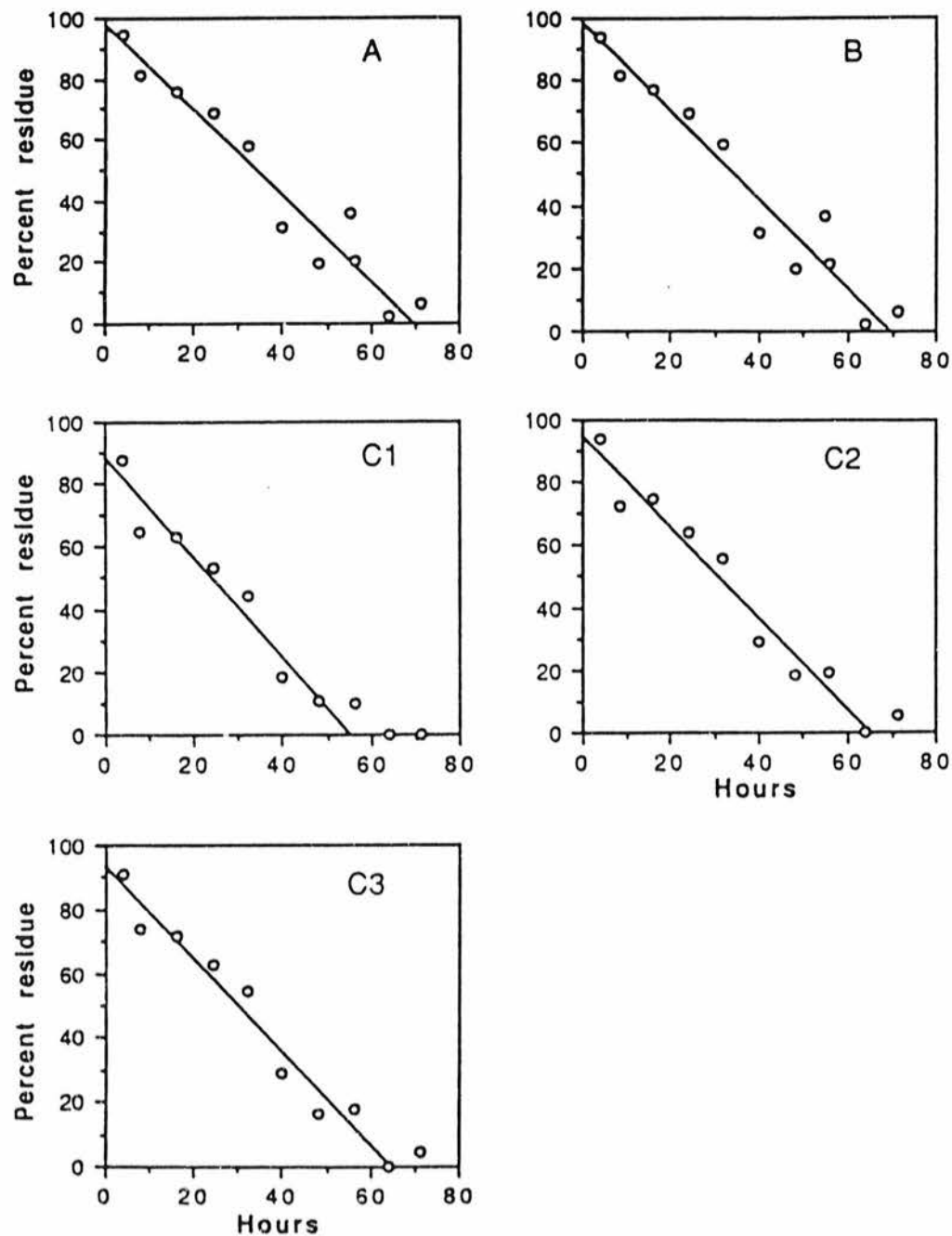
Figure 12. Residual curves of five constituents of polymeric MDI in vigorous stirring experiment. The straight line indicate linear regression curves to zero-order reaction equation. Test conditions: Nominal concentration; 1000mg/l, Stirring speed; 200rpm, Temperature; 25°C.

28
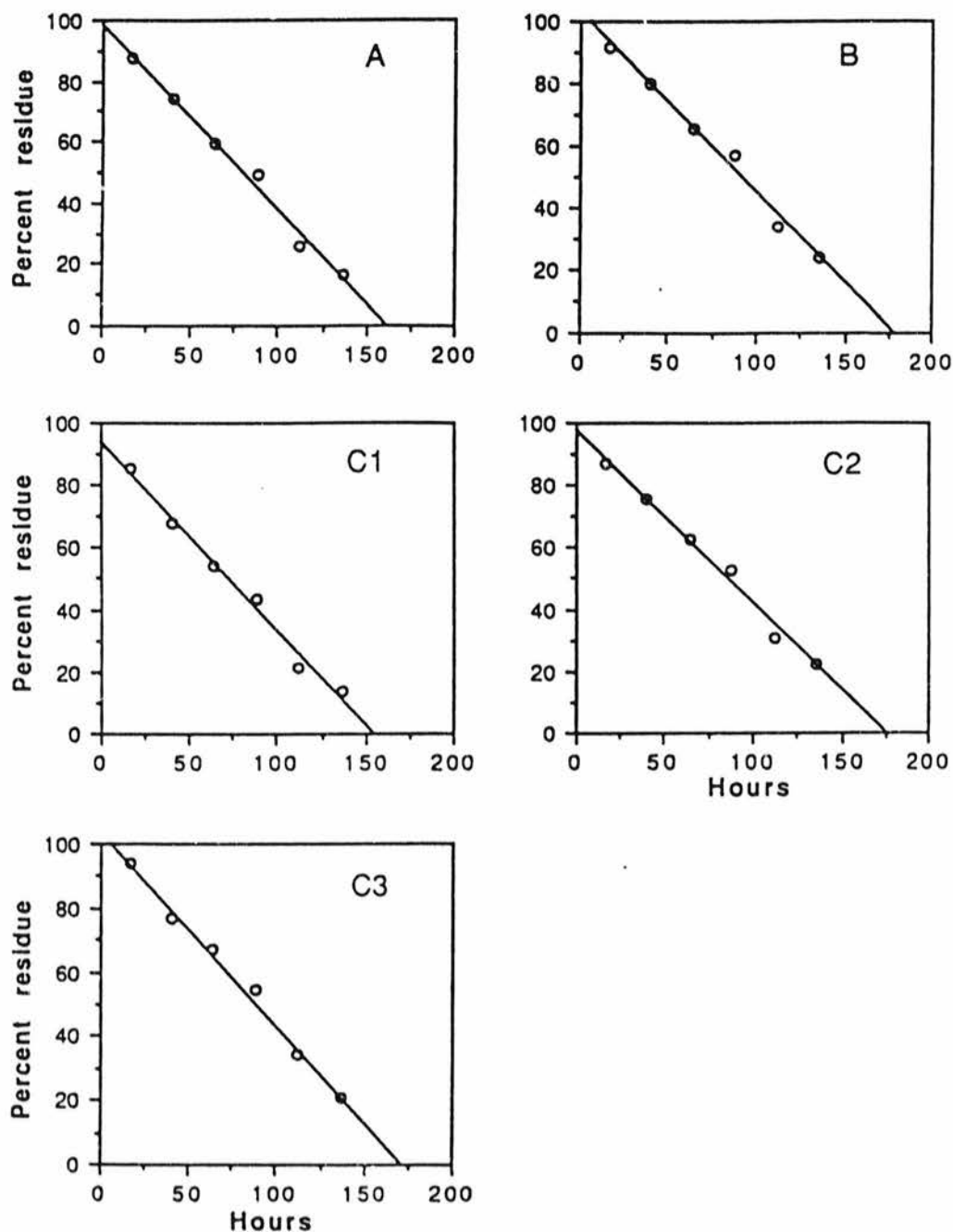
Figure 13. Residual curves of five constituents of polymeric MDI in vigorous stirring experiment. The straight line indicate linear regression curves to zero-order reaction equation.
Test conditions; Nominal concentration; 1000mg/l, Stirring speed; 1500rpm, Temperature; 12°C.
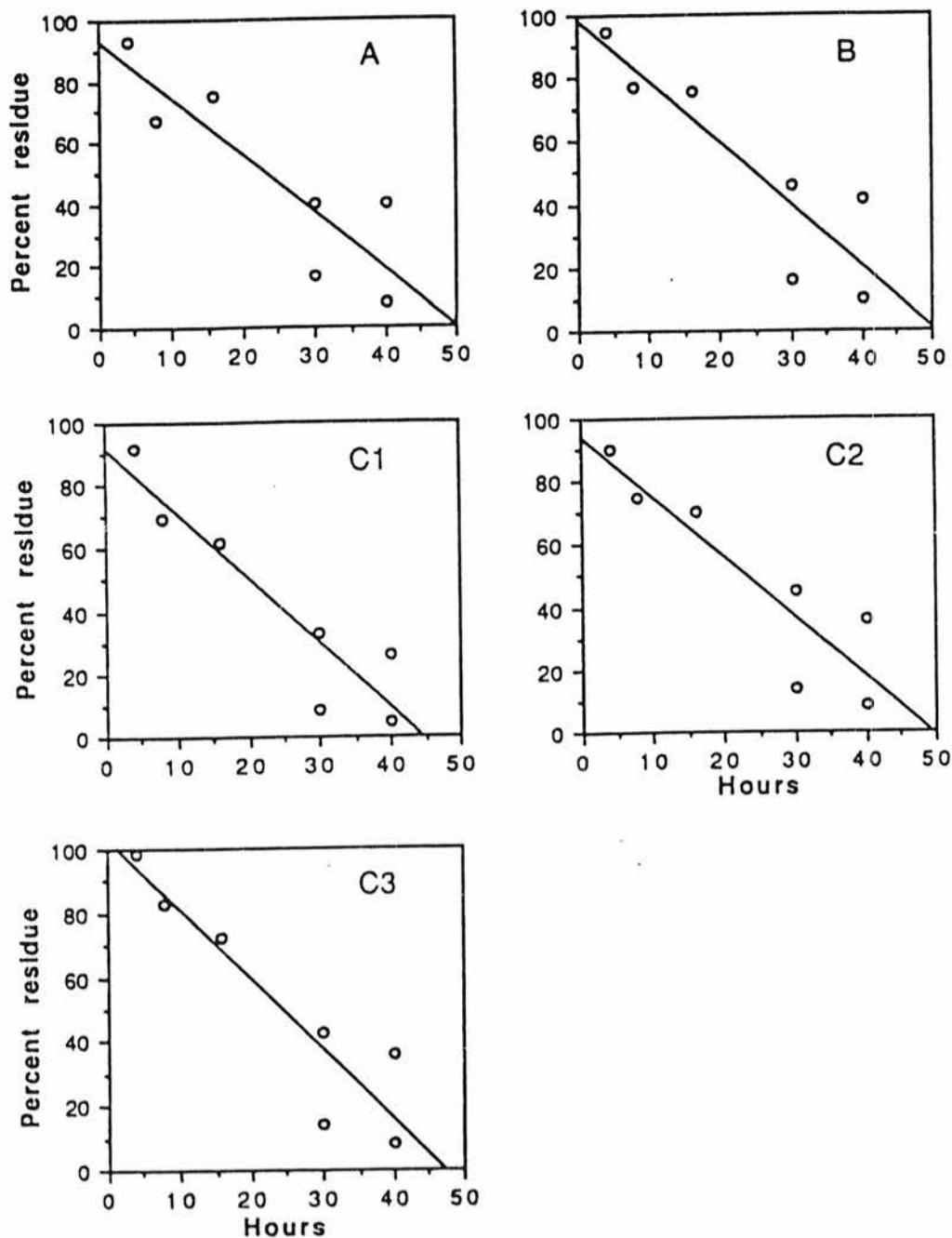
Figure 14. Residual curves of five constituents of polymeric MDI in vigorous stirring experiment in artificial sea water. The straight line indicate linear regression curves to zero-order reaction equation. Test conditions; Nominal concentration; 1000mg/l, Stirring speed; 1500rpm, Temperature; 25°C.

30
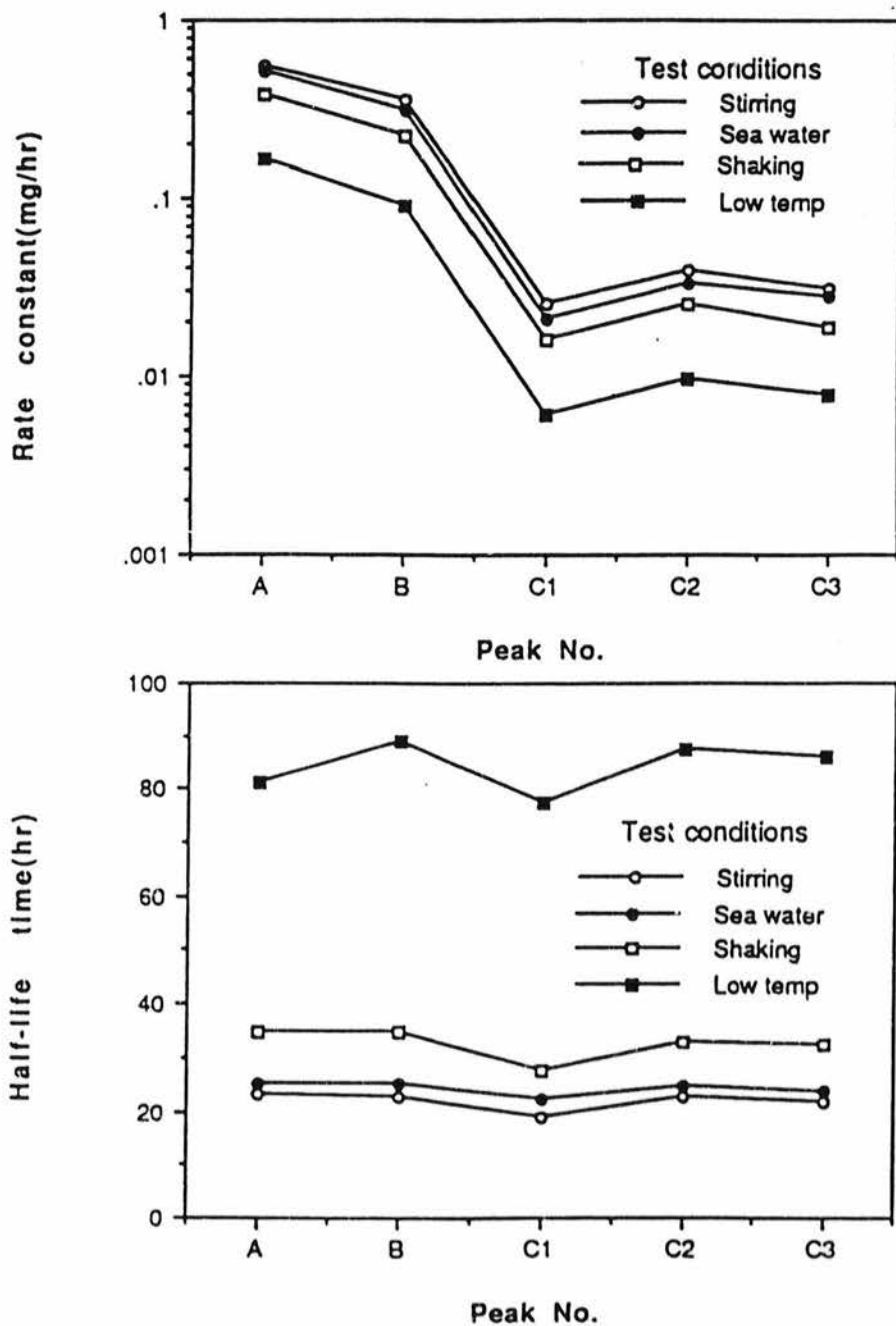
Figure 15. Comparisons of zero-order disappearance rate constant (**upper**), half-life time (**bottom**) among five constituents of polymeric MDI in vigorous stirring experiment.
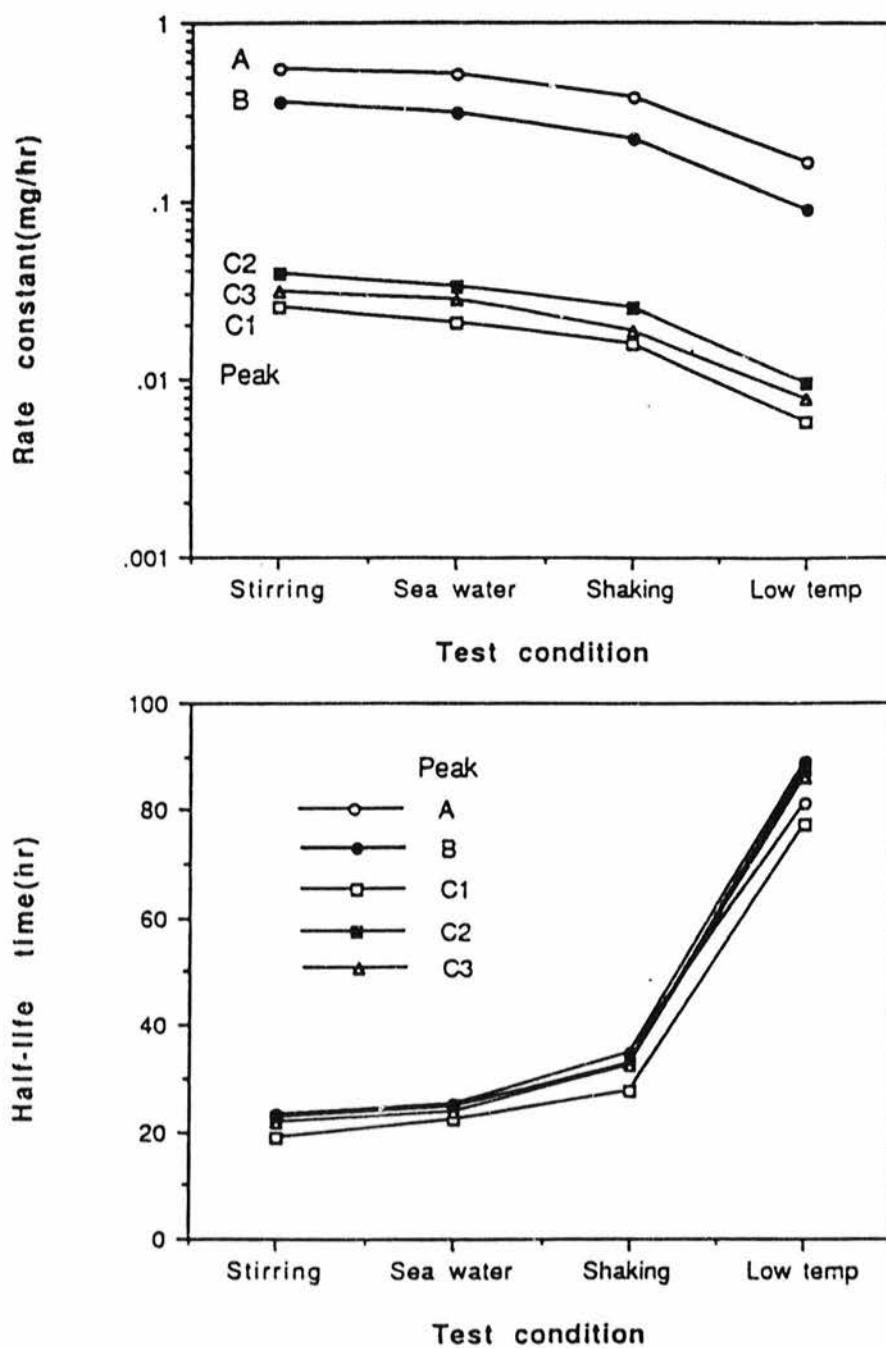
Figure 16. Comparisons of zero-order disappearance rate constant (upper), half-life time (bottom) of five constituents of polymeric MDI among four conditions in vigorous stirring experiment.

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3.1.2 Production of 4,4'-MDA and other water-soluble reaction products

Water-soluble reaction products is primary possible origin chemical for the toxicity to aquatic organism. Polymeric MDI reacts with water to produce 4,4'-MDA, which reacts with other polymeric MDI to produce oligoureas. 4,4'-MDA and oligoureas are thought to be main component of water-soluble reaction products of polymeric MDI in water. In this study, in order to estimate the kinetics and extent of the production of water-soluble reaction products, the time courses of 4,4'-MDA and DOC were measured. Figure 17 shows typical production curves of 4,4'-MDA and DOC under vigorous stirring condition. Both values were constant within experimental error after 6th-hour until the end of the experiment. DOC was higher about three times than 4,4'-MDA. This result suggests the existence of water-soluble reaction products other than 4,4'-MDA. In order to find the water-soluble reaction products other than 4,4'-MDA, the test solution was analysed by spectrophtometry and high performance liquid chromatograhpy, but UV spectrum of the test solution after 92 hours was nearly the same as that of 4,4'-MDA (Figure 19) and any new peak attributing to water-soluble reaction products other than 4,4'-MDA was not observed on ODS column under various elution conditions.

Figure 18 shows time course of 4,4'-MDA production under three nominal concentration of polymeric MDI. The concentration of 4,4'-MDA was nearly constant after 16th-hour at 1000mg/l nominal concentration of polymeric MDI, while at 10000mg/l nominal concentration of polymeric MDI, it increased from 6 hour to 22 hour, but it was smaller at 55 hour than at 22 hour. The final concentration of 4,4'-MDA at each nominal concentration was calculated by averaging last three values of the production curve of 4,4'-MDA in Figure 18. Figure 20 shows the relation-

ships between the final concentration of 4,4'-MDA and the nominal concentration of MDI and between the final fraction of MDI transformed to 4,4'-MDA in MDI added and the nominal concentration of MDI. The final concentration of 4,4'-MDA slightly increased, but the final fraction of MDI transformed to 4,4'-MDA decreased with increasing nominal concentration. Less than 0.5% of MDI added was transformed to 4,4'-MDA at the nominal concentration of MDI of 400mg/l or above (Figure 20).

Figure 21 shows the comparisons of the production curves of 4,4'-MDA production and the final concentration of 4,4'-MDA among four vigorous stirring experiments. The concentration of 4,4'-MDA reached to the constant values after about 40 hours in all experiments. It can be seen from Figure 21 that the gentle agitation and the salinity of the test solution slightly lowered the production of 4,4'-MDA, but the temperature of the test solution seems not to affect the production of 4,4'-MDA. These results indicate that the production of 4,4'-MDA is accelerated by increasing the strength of agitation and is depressed by the existence of salt in test solution.
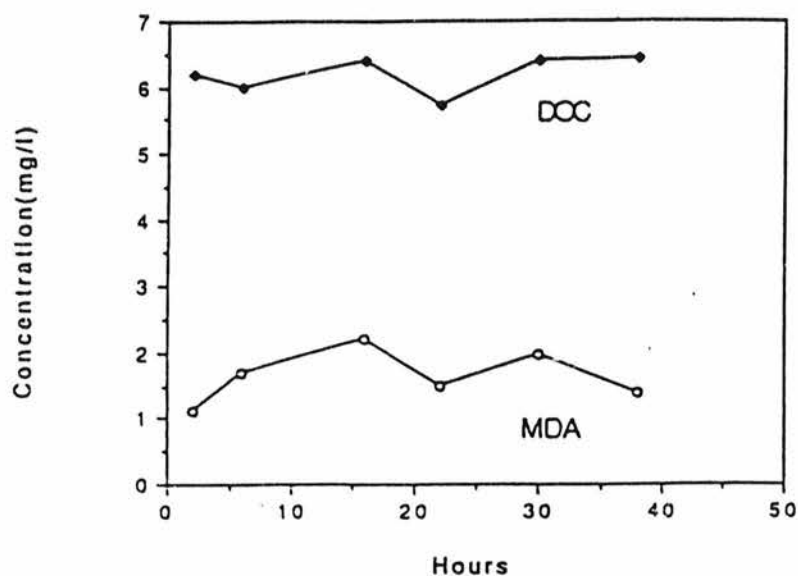
Figure 17. Prodluction curves of 4,4'-MDA and DOC in vigorous stirring experiment. Test conditions: Nominal concentration; 400mg/l, Stirring speed; 1500rpm, Temperature; 25°C.
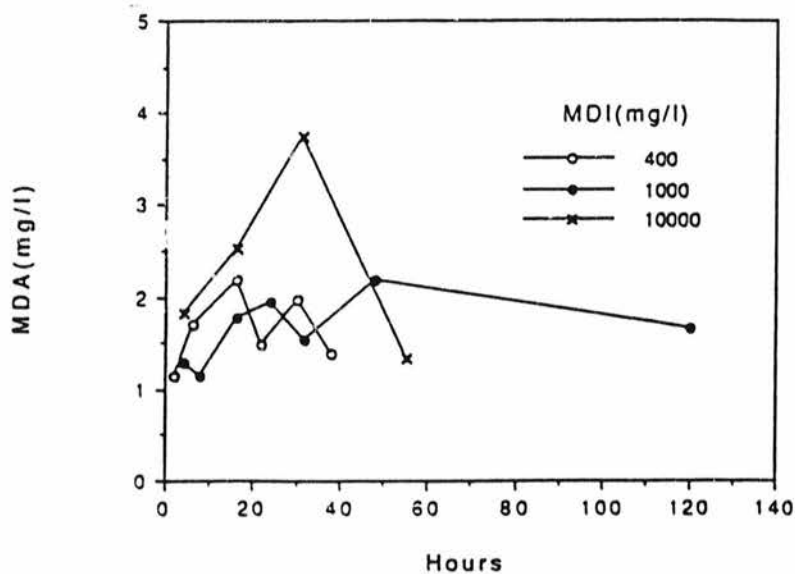
Figure 18. Production curves of 4,4'-MDA in three vigorous stirring experiments. Test conditions: Stirring speed; 1500rpm, Temperature; 25°C.

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Polymeric MDA
1.3 mg/l

4,4'-MDA
1.1 mg/l

Test solution
after 92 hrs

36
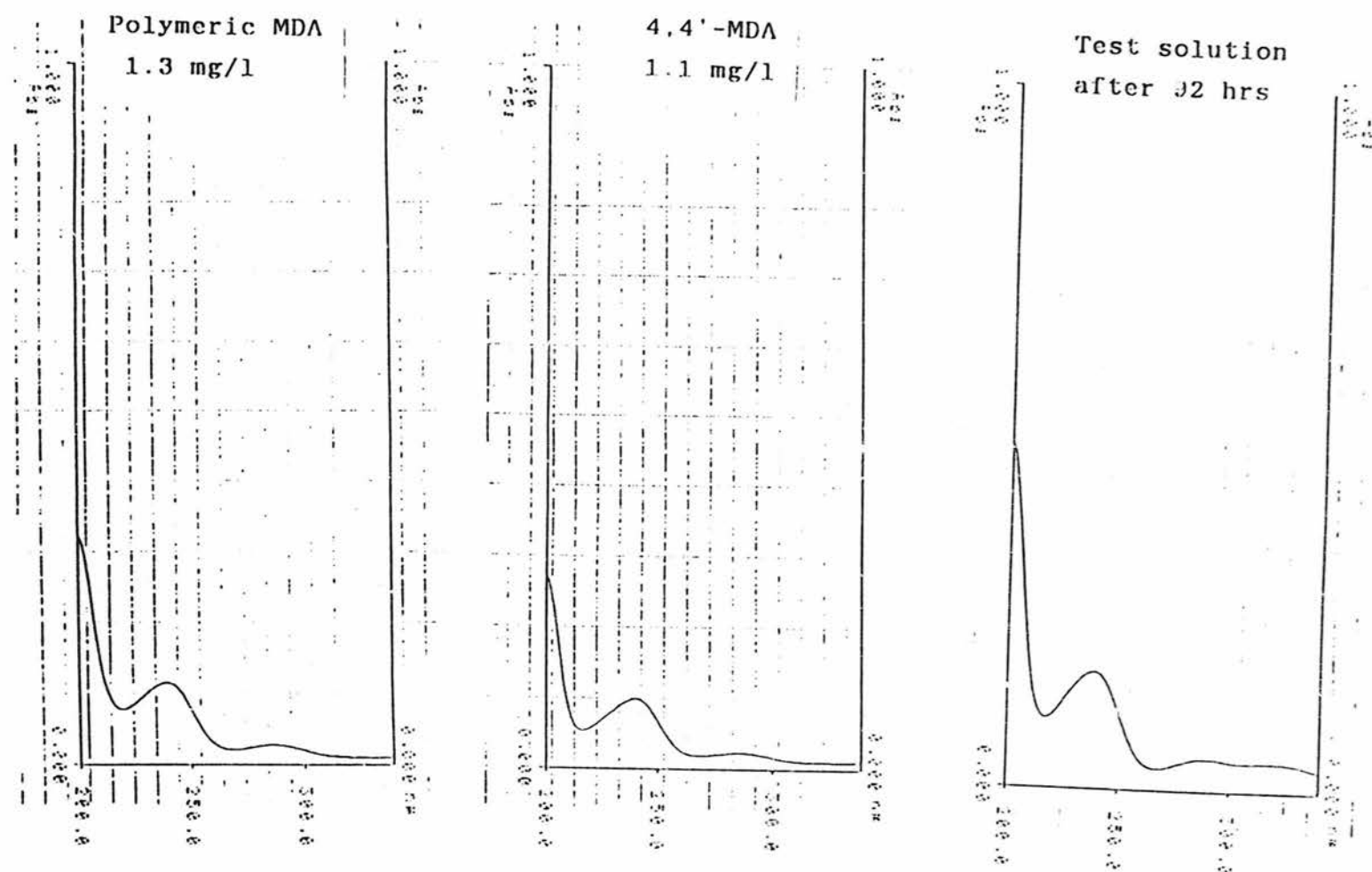
Figure 19. Comparison of UV spectra of test solution after 92 hours in vigorous stirring experiment with that of the standard solution of polymeric MDA and 4,4'-MDA.

Test condition: Nominal concentration; 1000mg/l, Stirring speed; 1500rpm, Temperature; 25°C.
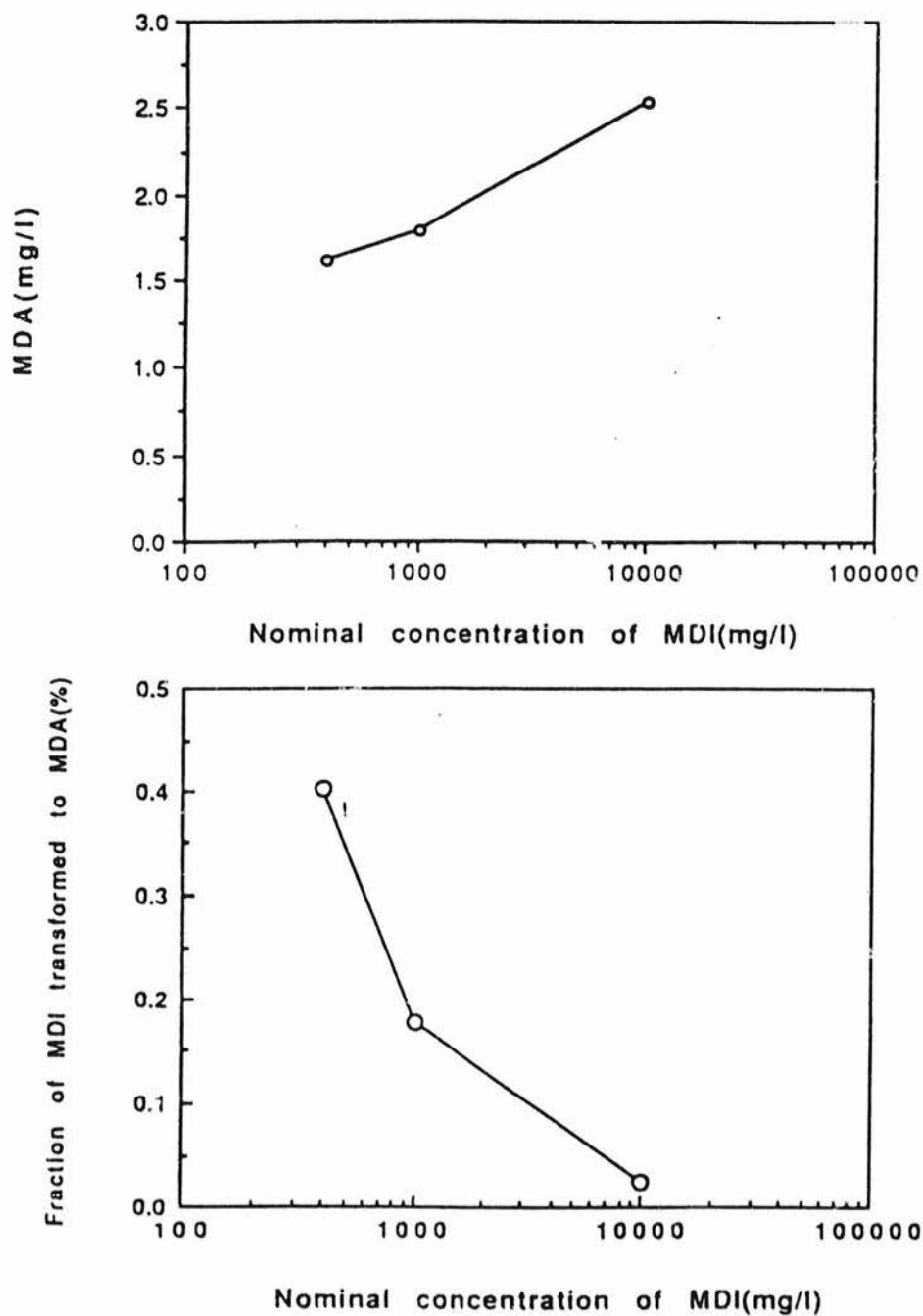
Figure 20. Relationships between the final concentration of MDA (upper), the final fraction of MDI transformed to MDA (bottom) and the nominal concentration of polymeric MDI in vigorous stirring experiment. The final fraction was calculated by the method described in the text.

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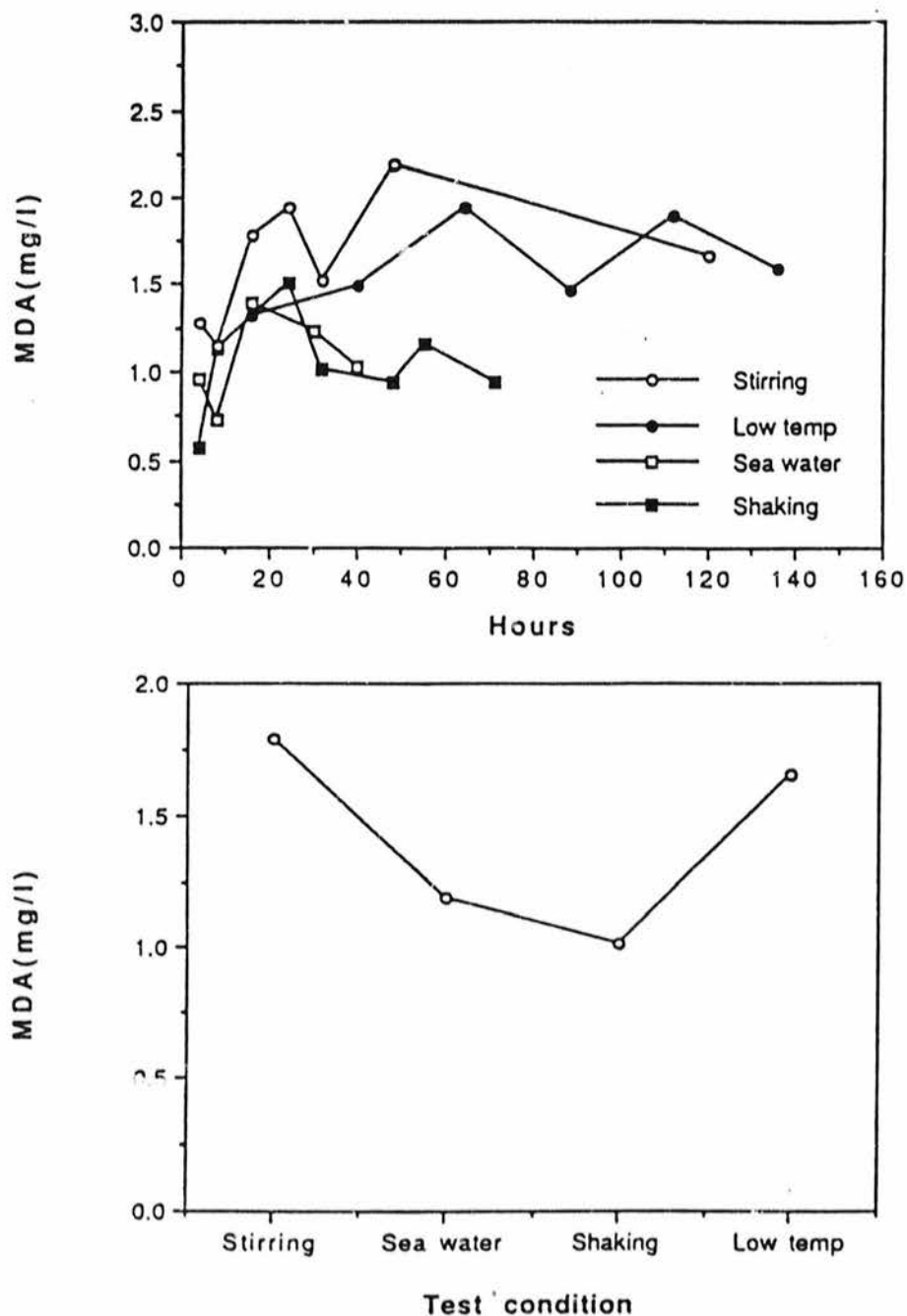
Figure 21. Production curves of MDA in four vigorous stirring experiments (**upper**) and the comparison of the final concentration of MDA among four conditions (**bottom**).

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3.1.3 Production of water-insoluble reaction products

The test substance changed from dark brownish liquid to pale yellow solid and the proportion of the reaction products insoluble in both water and toluene increased with time. The final reaction products was not completely soluble in DMF containing 10mM of LiCl. Figure 22 shows the variation in GPC profile of the water-insoluble reaction products soluble in this solvent together with that of DBA derivative of polymeric MDI for reference. The peak of the products shifted to short retention time with time, indicating that the reaction products was polymerized to polyurea of higher molecular weight insoluble to usual organic solvents such as toluene and DMF.

The proportion of the substance soluble in LiCl-DMF to total water-insoluble reaction products was determined in duplicates by HPLC using DBA derivative of polymeric MDI as a standard for the quantification as shown in 2.2.1(3). The result is shown in Table 4. Average proportion was 6.6%.

It is concluded from the results of 3.1.2 and 3.1.3 that under vigorous stirring condition at the nominal concentration of MDI of 400mg/l or above, only less than 0.5% of polymeric MDI added is finally transformed to 4,4'-MDA (Figure 20), which is major water-soluble reaction products, and the remaining polymeric MDI is transformed to the water-insoluble substance, only 6.6% of which is soluble in LiCl-DMF (Table 4). Therefore more than 92.9% (= 100 - 0.5 - 6.6) of polymeric MDI added is thought to be finally transformed to the substance insoluble to water and usual organic solvent.

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After 48hrs

After 32hrs

After 20hrs

After 4hrs

Standard DB.-MDI
100mg/l
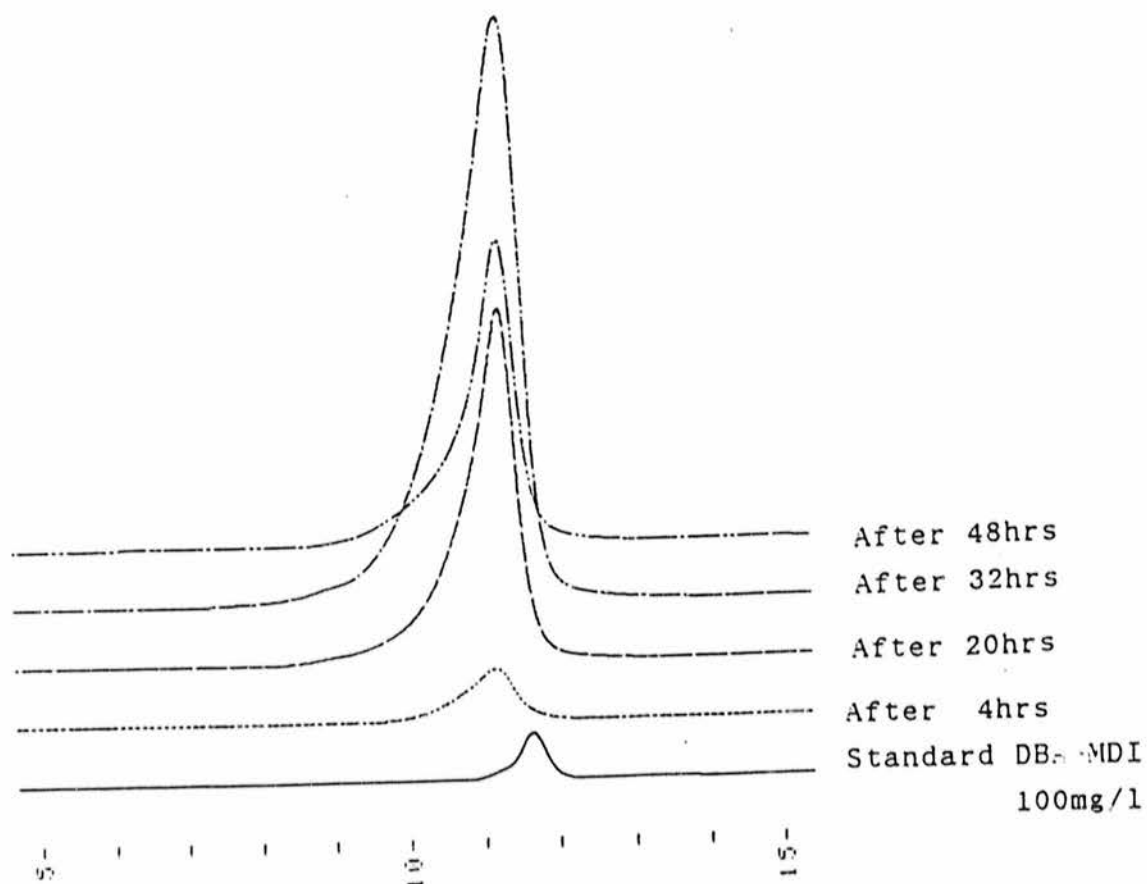
Figure 22. Variation in GPC profile of the water-insolube reaction product soluble to LiCl-DMF in vigorous stirring experiment. Test conditions: Nominal concentration; 1000mg/l, Stirring speed; 1500rpm, Temperature; 25'C.

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Table 4 Fraction of the substance soluble in LiCl-DMF
to total water-insoluble reaction products ̇ polymeric MDI

Experimental	Fraction (%)		
condition	1	2	Average
Vigorous stirring	8.1	5.0	6.6
Static	0.8	0.6	0.7

The proportion was determined by the method of 2.2.1(3)
and 2.2.2(3).

3.2 Static experiment

3.2.1 Kinetics of the disappearance of polymeric MDI

Figure 23 shows the variation in the chromatograms of DBA
derivatives of the residual test substance along with that of the
standard solution. All peaks diminished simultaneously with time
similarly to vigorous stirring experiment and the same intermedi-
ate substances were observed.

The experiments were carried out with three interfacial
areas between water and polymeric MDI phases in order to eluci-
date the mechanism of the reaction between polymeric MDI and
water. The residual curves for five constituents of polymeric MDI
under three conditions were shown in Figure 24 to 25. The per-
cent residue for all constituents decreased linearly with time in
the experiments of the interfacial area of 13.2 cm^2 and 18.1 cm^2,
while they decreased linearly with time until 20 % after 10 days,
its value kept thereafter until 20 days in the experiment of the

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interfacial area of 5.72 cm^2. The test substance changed in the appearance from transparent liquid to opaque solid downward from the interfacial between water and polymeric MDI phases with time. The change stopped at about half depth in the experiment of the interfacial area of 5.72 cm^2, while it proceeded to the bottom in other two experiment. These results indicate that water can not permeate until a fixed depth of polymeric MDI phase from the interfacial probably because the reaction products repels water.

The slope of the linearly decreased part of the residual curve was determined by least squares method and the rate constant of zero-order reaction kinetics and half-life time were calculated by equations 2 and 3. The slopes for five constituents were nearly identical, and they increased linearly with the interfacial area (Figure 27). Figure 28 shows the variations of rate constant and half-life time with the interfacial area and Figure 29 shows the variations of them with the kind of the constituent. The rate constant was larger with higher content of the constituent and it increased linearly with increasing inter-facial area between water and polymeric MDI phases, while half-life time decreased linearly with the interfacial area, but it was not dependent on the kind of the constituent. These results indicate that the disappearance reaction of polymeric MDI pro-ceed from the interfacial to the bottom with accompanying permea-tion of water into polymeric MDI phase through the interfacial.

3.2.2 Production of 4,4'-MDA and other water-soluble reaction products

Figure 30 shows the production curves of 4,4'-MDA and the relationship between the final concentration of 4,4'-MDA and the interfacial area. The same figure for DOC is shown in Figure 31. The concentration of 4,4'-MDA increased gradually until 7th-day

and reached to constant value in all experiments. The final concentration of 4,4'-MDA, which was calculated by averaging last three values of the production curve of MDA in Figure 30, was less than one third of that in vigorous stirring experiment and was almost independent on the interfacial area. DOC was over 4 times larger than 4,4'-MDA, but there was not definite relationship between the final concentrations of 4,4'-MDA and DOC. The final amount of MDI transformed to MDA was less than 0.005% of MDI added,[1] and total amount of water-soluble reaction products estimated from DOC value was less than 2 mg which corresponded to 0.04% of polymeric MDI added.[2]

UV spectrum of the test solution after 14th-day was not consistent with that of 4,4'-MDA, indicating the existence of water-soluble reaction products other than 4,4'-MDA (Figure 32). Water-soluble reaction products other than 4,4'-MDA were also observed on ODS column under the same elution condition, but the identification was not difficult because of low concentration of them (Figure 33).

[1] The final fraction of polymeric MDI transformed to 4.4'-MDA in polymeric MDI added. F_{MDA}(%). was calculated by the following equation:

$F_{MDA} = C_{MDA} / K_{MDA} * V / 1000 / A * 100$

where C_{MDA}(mg/l). K_{MDA}. V(ml) and A(mg) are the final concentration of 4.4'-MDA. the ratio of molecular weights of 4.4'-MDA and polymeric MDI. the volume of the test solution and total amount of MDI added. Since C_{MDA} is less than 0.6mg/l from Figure 30. K_{MDA} is 0.82. (molecular weight of polymeric MDI is calculated on the assumption that the content of NCO in polymeric MDI is 31.1%). V is 300ml and A is 5000mg. F_{MDA} become to be

$F_{MDA} < 0.6 / 0.82 * 300 / 1000 / 5000 * 100 = 0.0043%$

[2] Total amount of water-soluble reaction products. P_{total}(mg). and the total fraction of polymeric MDI transformed to water-soluble reaction products in polymeric MDI added. F_{to-}

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$_{tal}$(%). were estimated from DOC(mgC/l) of test solution by the following equations:

P_{total} = DOC / K_c * V / 1000   and

F_{total} = P_{total} / A * 100

where K_c. V(ml) and A(mg) are carbon content of polymeric MDI. volume of test solution and total amount of polymeric MDI added. respectively. Since K_c is 0.735. which is calculated on the assumption that the content of NCO in polymeric MDI is 31.1%. V is 300ml. A is 5000mg and DOC was less than 5mgC/l from Figure 31. P_{total} and F_{total} become to be

P_{total} < 0.5 / 0.735 * 300 / 1000 = 2.0mg   and

F_{total} < 2.0 / 5000 * 100 = 0.04%

3.2.3 Production of water-insoluble reaction products

As MDI disappeared, the toluene-insoluble reaction products increased. No peak of the toluene extract was detected on ODS column after 13th-day in the experiments of 13.2 cm^2 and 18.1 cm^2 interfacial area. These results indicate that all of the reaction products of MDI insoluble to water finally become insoluble to toluene. In order to examine the nature of the final reaction products of MDI, GPC profile of the toluene-insoluble reaction products was analyzed and the solubility to organic solvents of the final products, which prepared by extending the experiment of 18.1 cm^2 interfacial area to 4 weeks as shown 2.2.2(3), were examined. Figure 34 shows the variation of GPC profile of the toluene-insoluble substance soluble in LiCl-DMF. The peak shifted to short retention time with time, indicating that the polymerization proceeded with time. The final products were insoluble to usual organic solvents such as chloroform, methanol, acetnitrile. The fraction of the products soluble in LiCl-DMF was only 0.7% (Table 4).

Consequently, it is concluded that polymeric MDI was trans-

formed to water-soluble substance at less than 0.04% of polymeric MDI added and the remaining polymeric MDI was transformed to the substance insoluble to toluene. Only 0.7% of the tolune-insoluble reaction products was dissolved in DMF containing LiCl and 99.7% of it is insoluble in both water and usual organic solvent including DMF-LiCl.
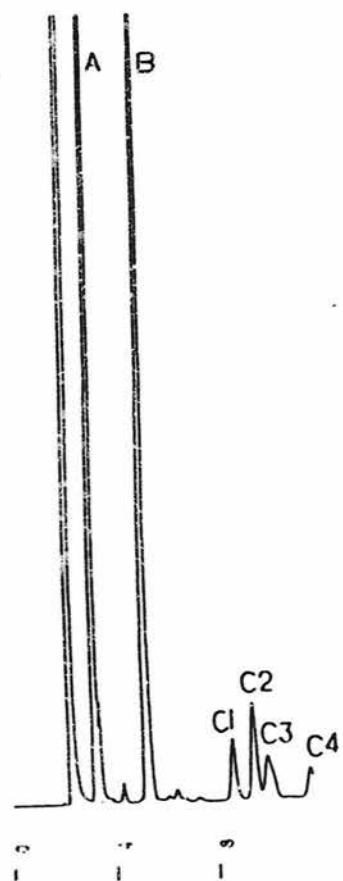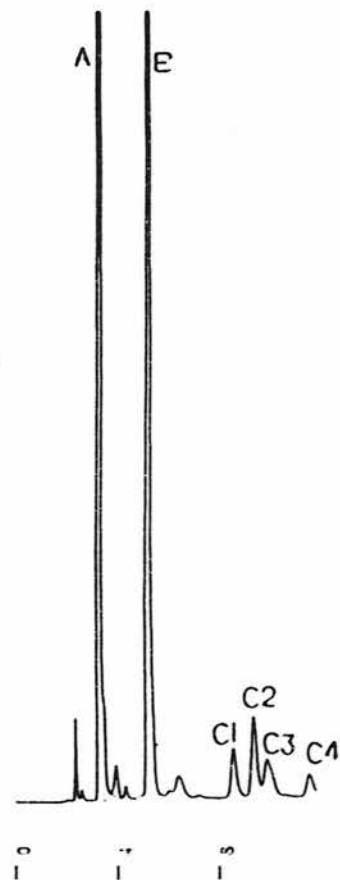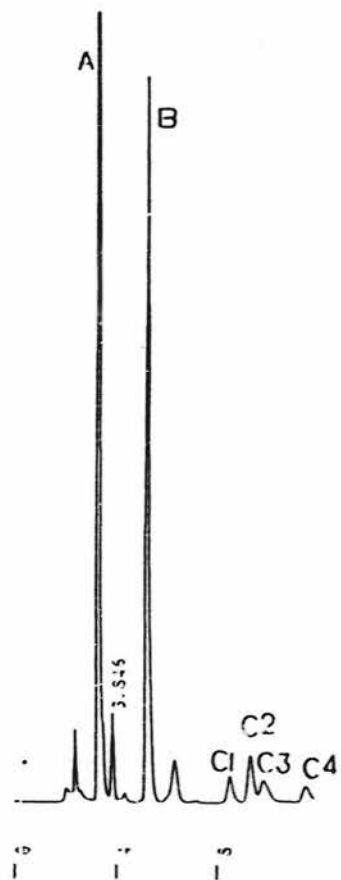
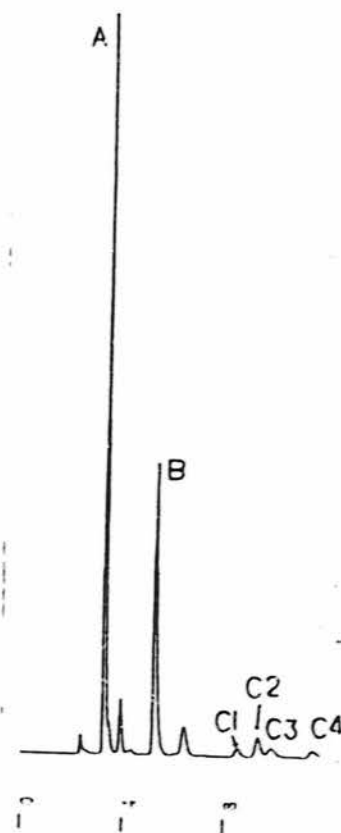Figure 23. Variation in chromatogram of DBA derivative of residu-
al substance in static experiment.

Test conditions: polymeric MDI;5g, Interface area between water-
polymeric MDI phases; 5.72 cm^2, Temperature; 25°C.
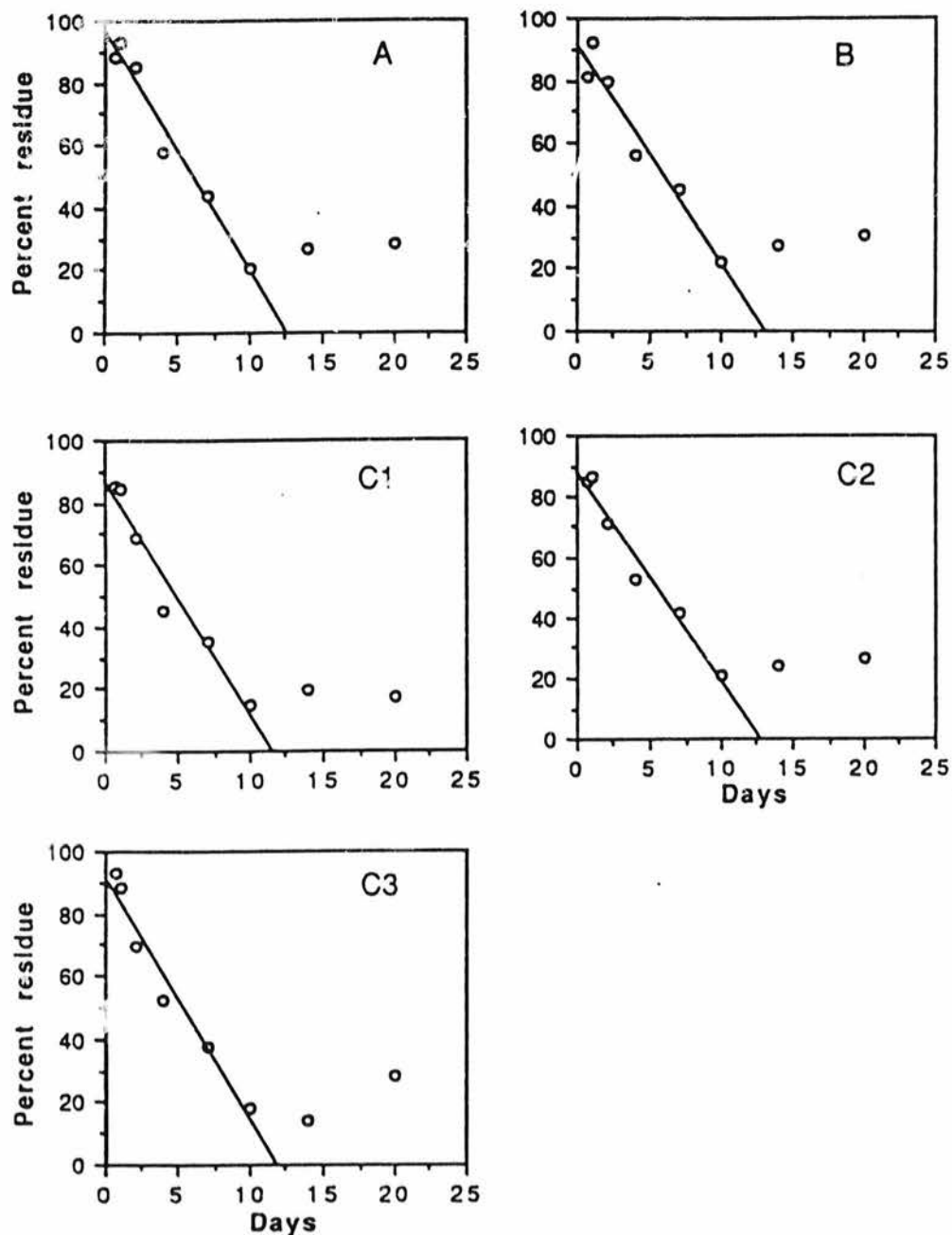
Figure 24. Residual curves of five constituents of polymeric MDI
in static experiment. The straight line indicate linear regres-
sion curves to zero-order reaction equation.
Test conditions: polymeric MDI; 5g, Interface area between water-
polymeric MDI phases; 5.72 cm^2, Temperature; 25°C.

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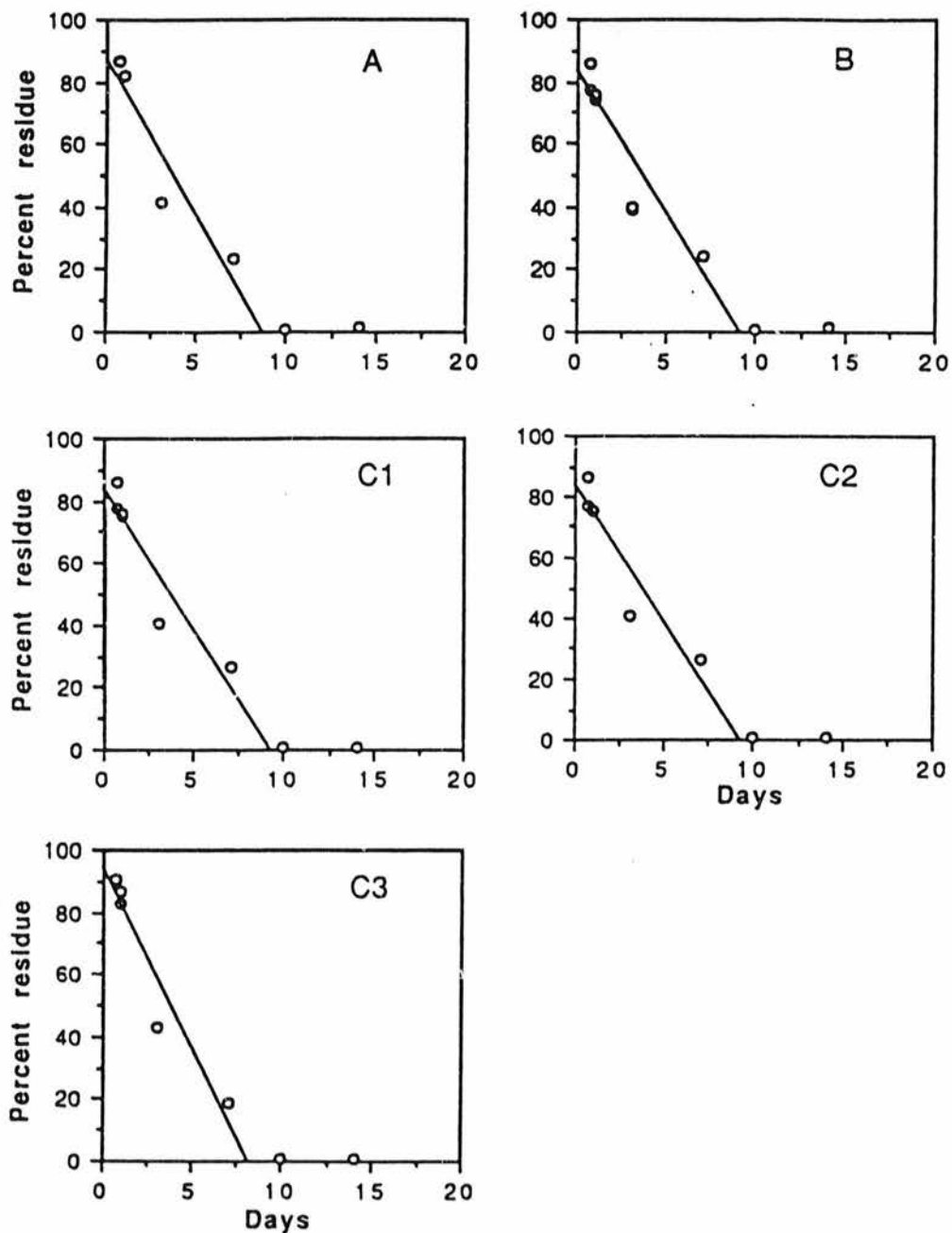
Figure 25. Residual curves of five constituents of polymeric MDI in static experiment in water. The straight line indicate linear regression curves to zero-order reaction equation.
Test conditions: polymeric MDI;5g, Interface area between water-polymeric MDI phases; 13.2 cm^2, Temperature; 25°C.

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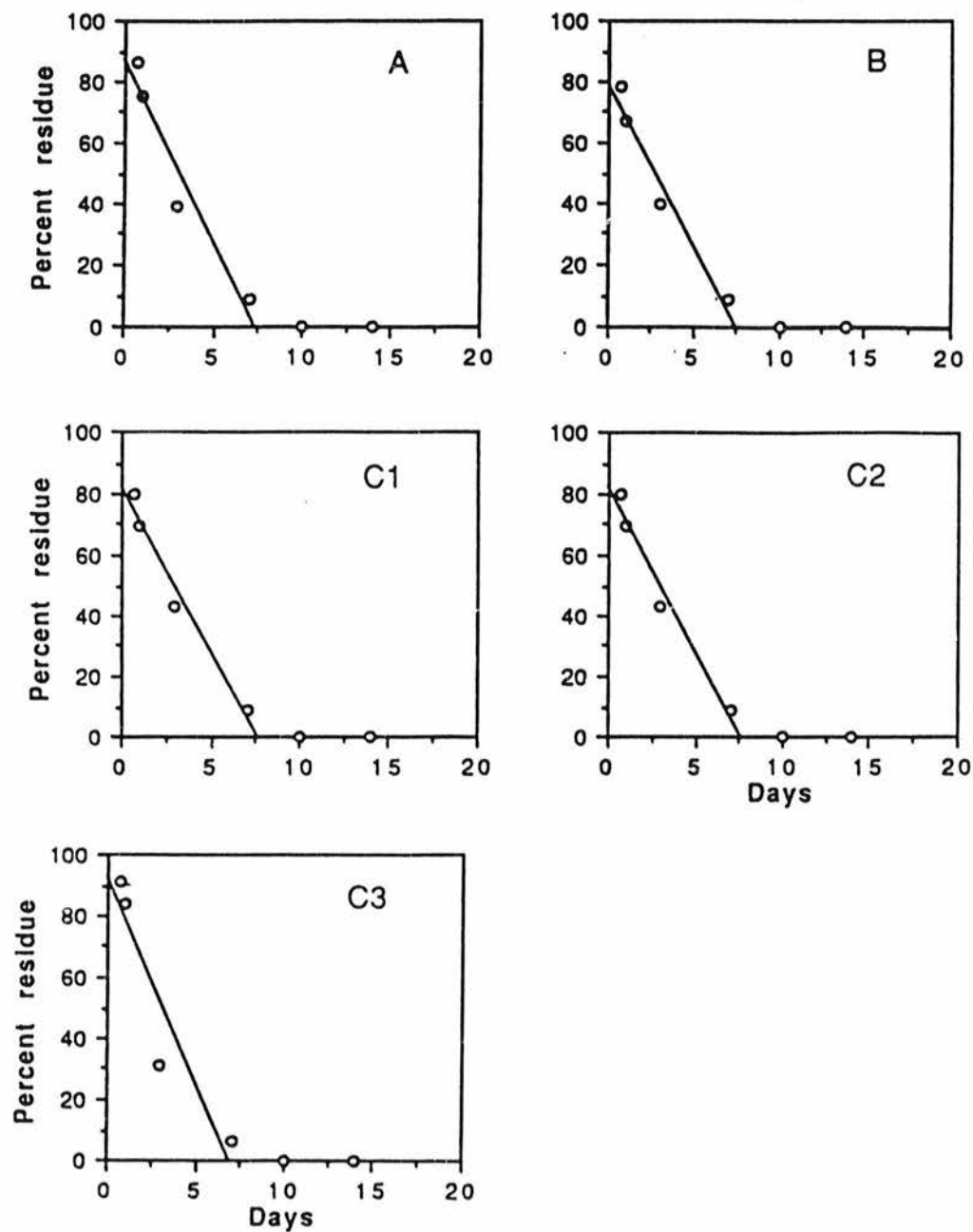
Figure 26. Residual curves of five constituents of polymeric MDI in static experiment in water. The straight line indicate linear regression curves to zero-order reaction equation.

Test conditions: polymeric MDI;5g, Interface area between water-polymeric MDI phases; 18.1 cm^2, Temperature; 25°C.

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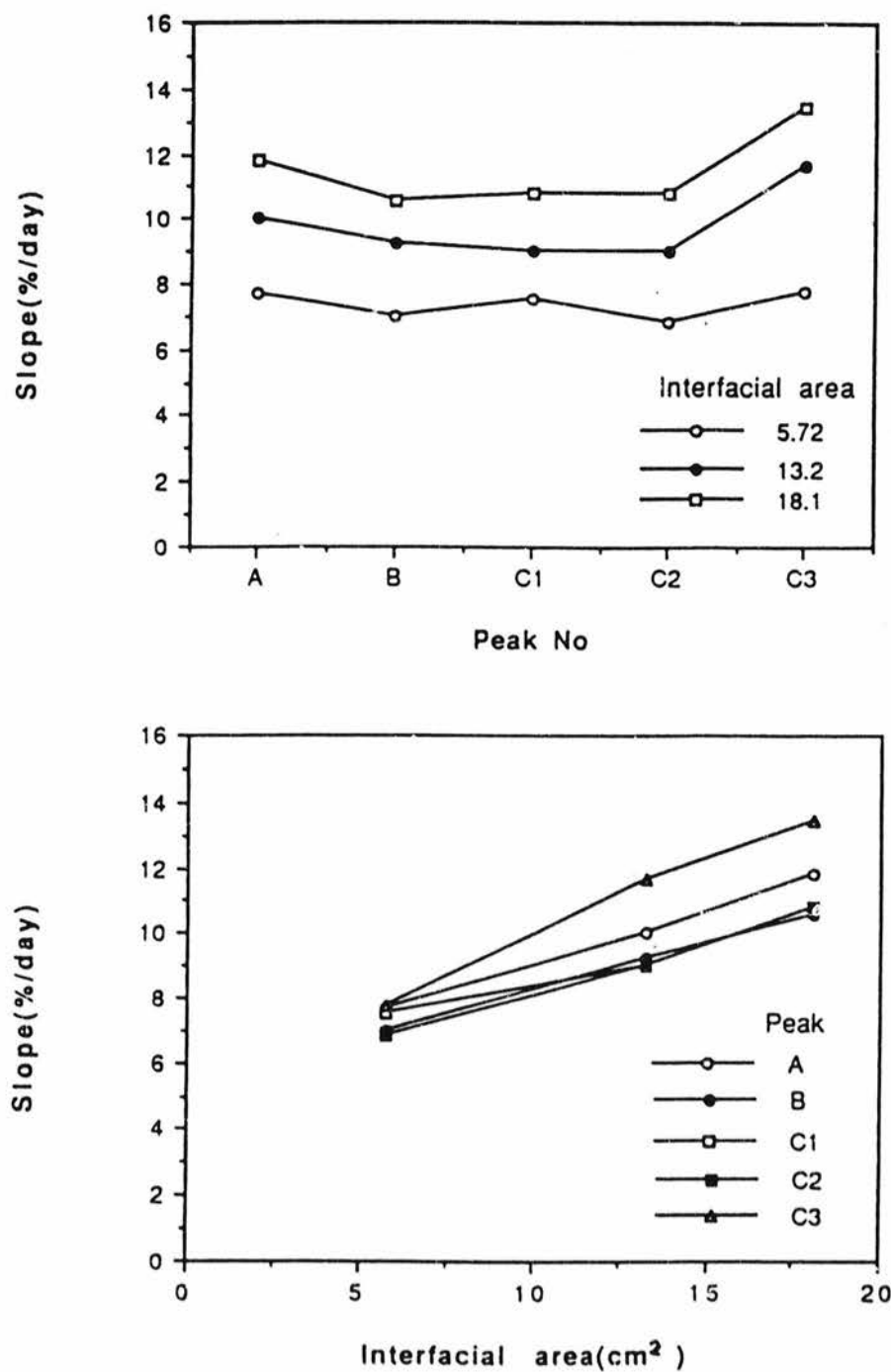
Figure 27. Comparison of slope of linear regression curves among five constituents of polymeric MDI (upper) and the relationship with the interfacial area (bottom) in static experiment.

50
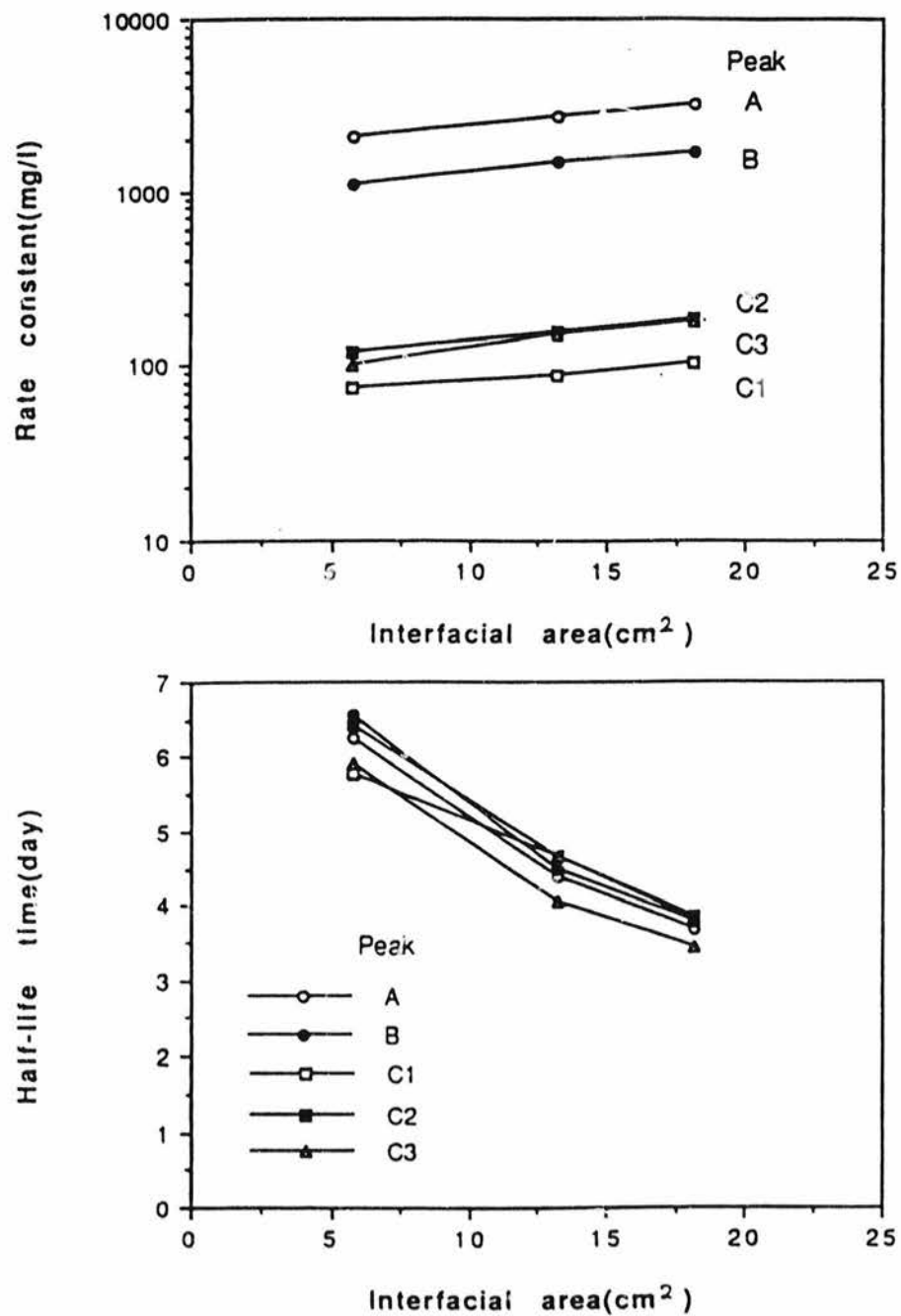
Figure 28. Relationships between zero-order disappearance rate constant (**upper**), half-life time (**bottom**) of five constituents of polymeric MDI and the interfacial area in static experiment.

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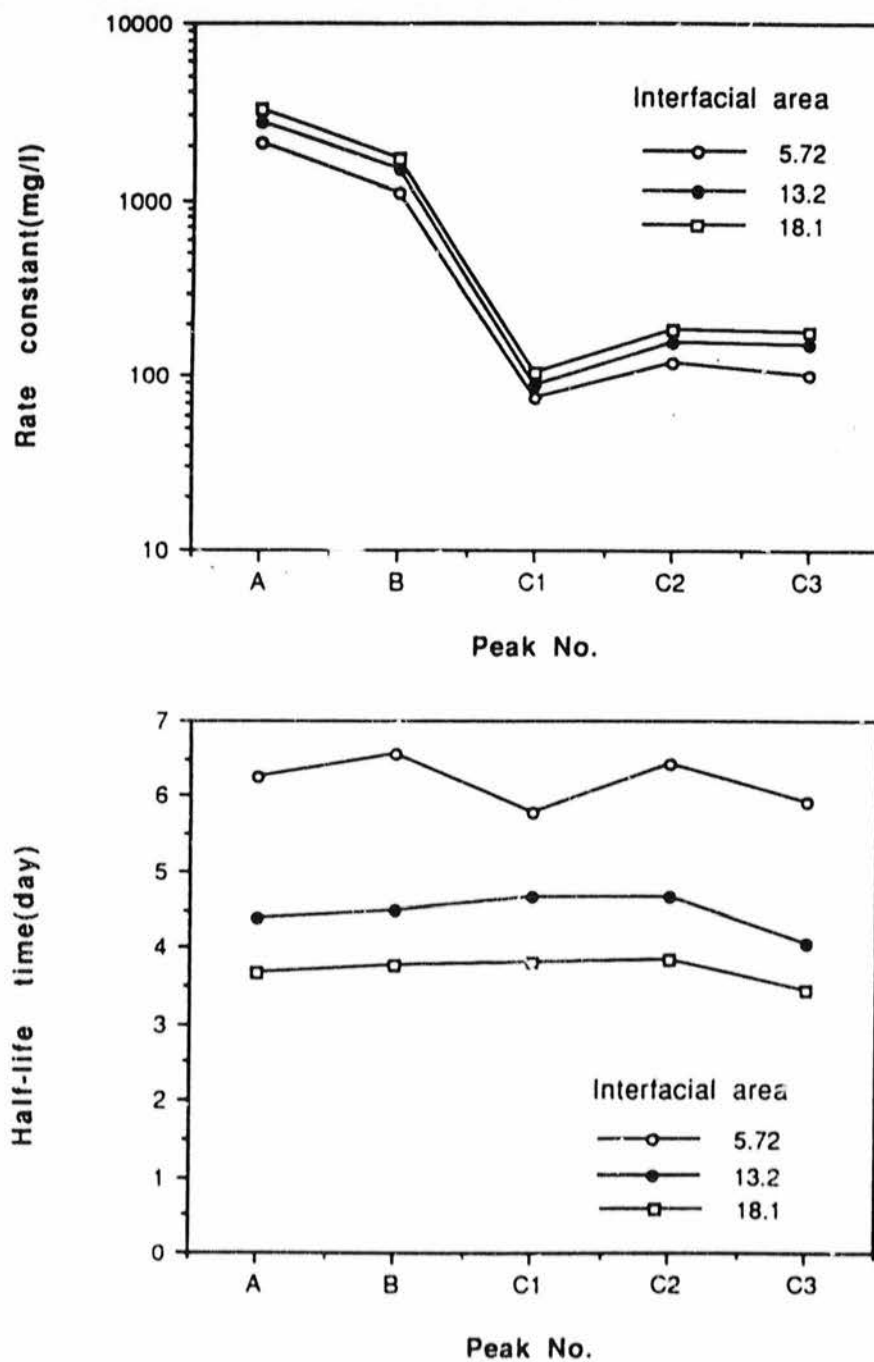
Figure 29. Comparisons of zero-order disappearance rate constant (upper), half-life time (bottom) among five constituents of polymeric MDI in static experiment.

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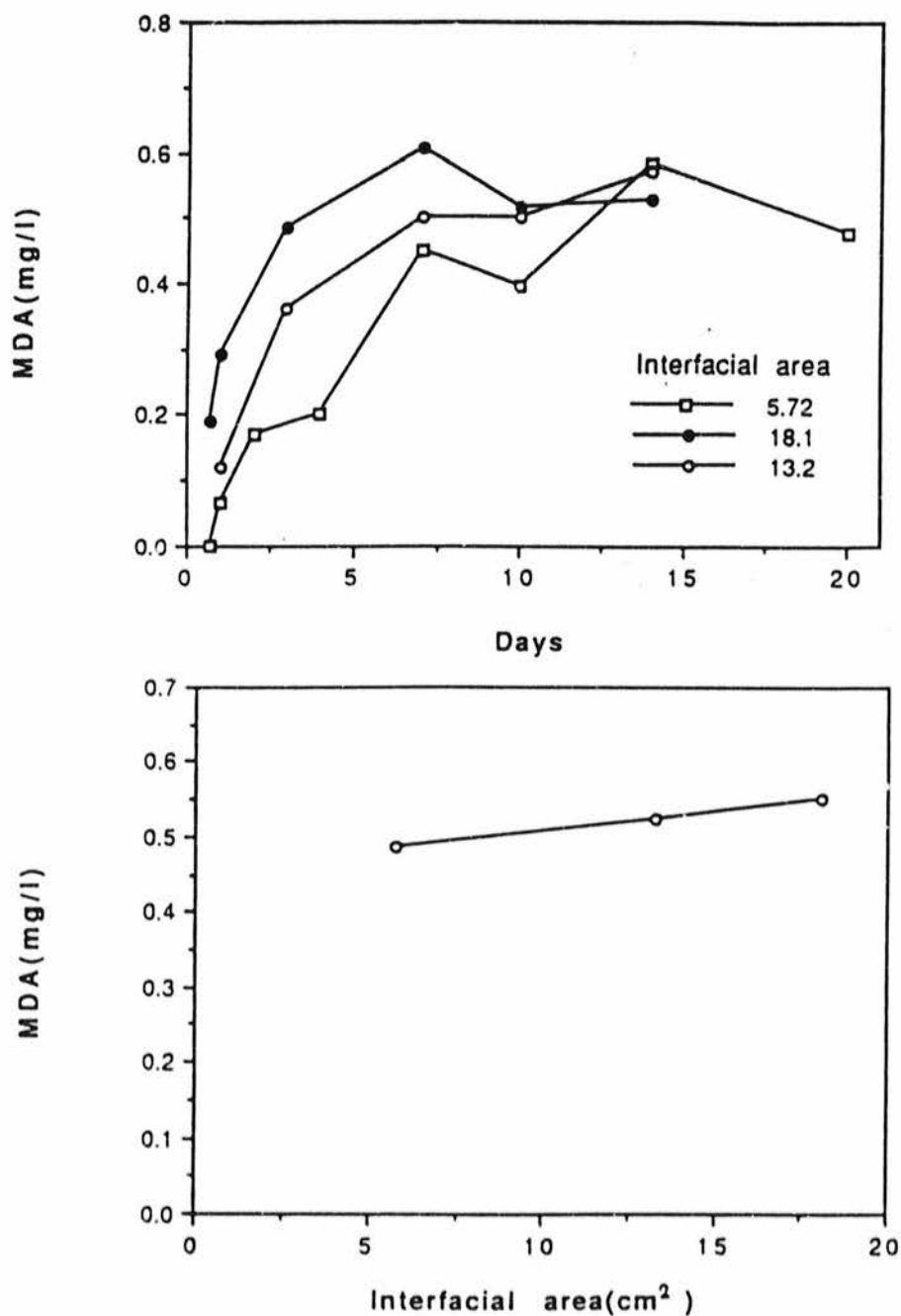
Figure 30. Production curves of MDA in three static experiments (upper) and the relationship between the final concentration of MDA and the interfacial area (bottom). The final concentration of MDA is the mean of last three values of the curve.

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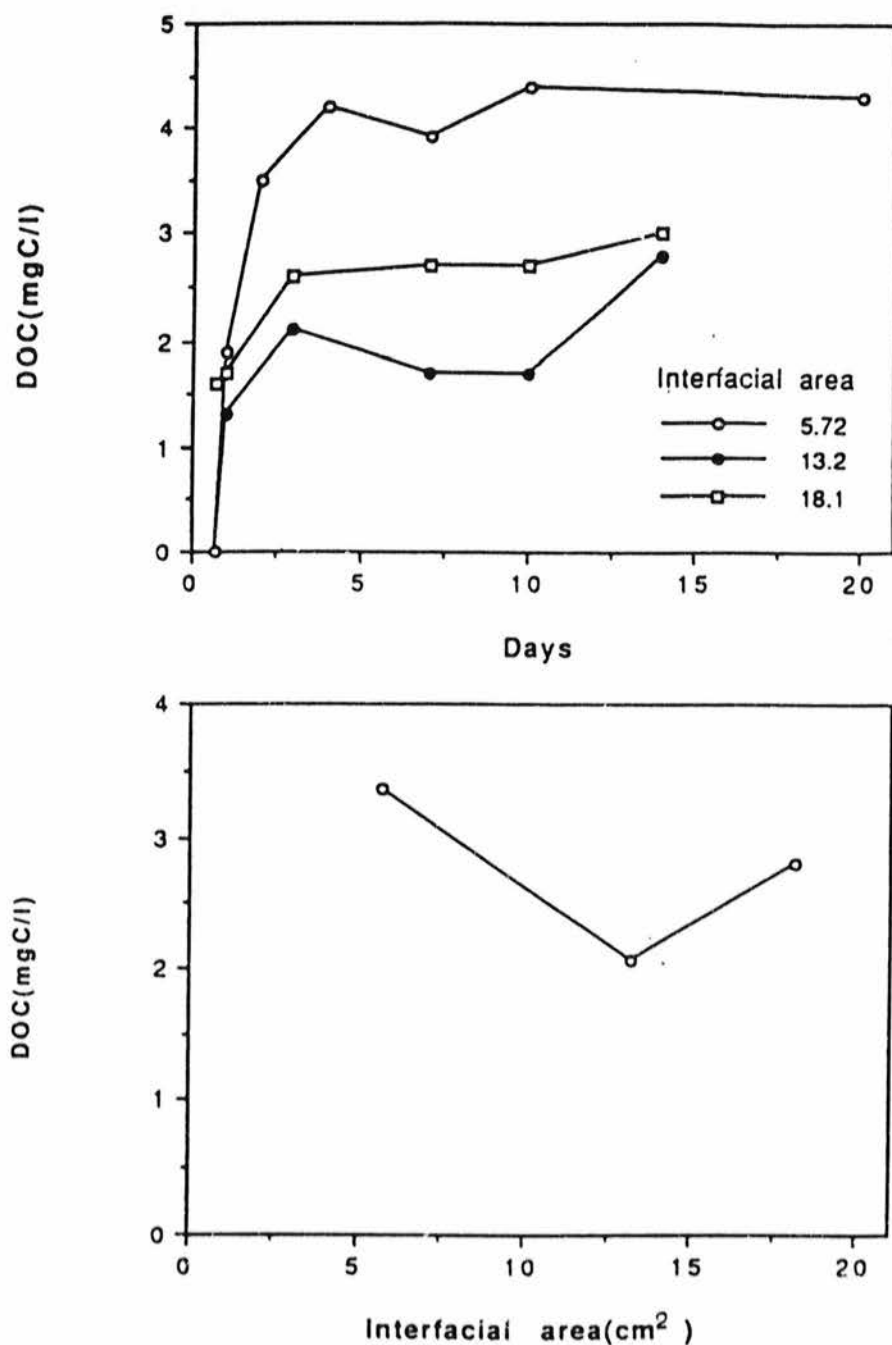
Figure 31. Production curves of DOC in three static experiments (upper) and the relationship between the final concentration of DOC and the interfacial area (bottom). The final concentration of DOC is the mean of last three values of the curve.

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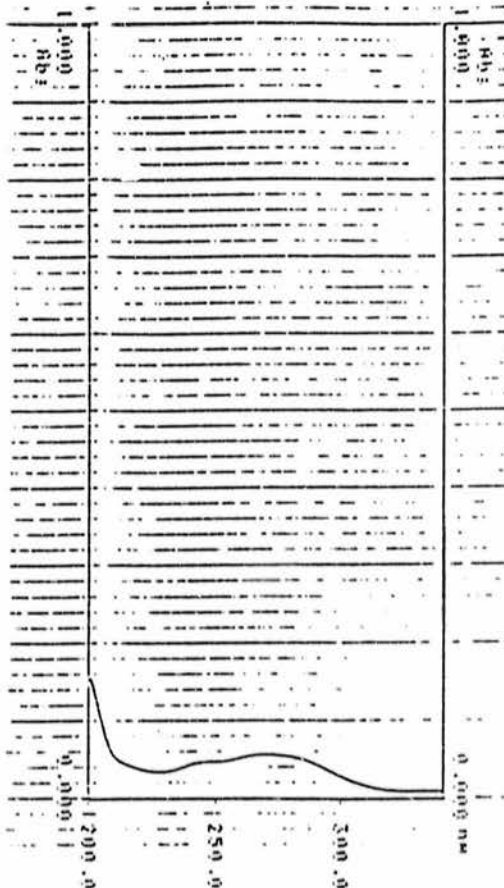
Standard 4,4'-MDA
1.01mg/l
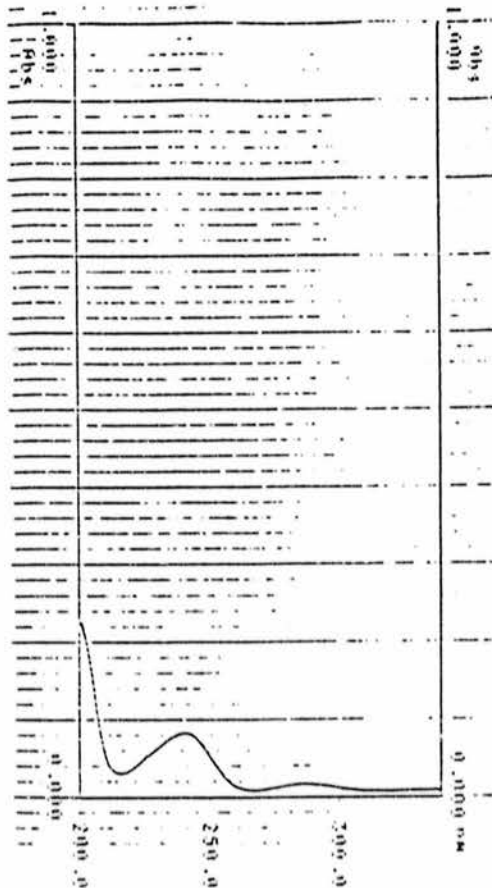
Test solution after 14 days

Figure 32. Comparison of UV spectra of test solution after 14days
in static experiment with that of standard solution of 4,4'-MDA.
Test conditions: polymeric MDI;5g, Interfacial area between
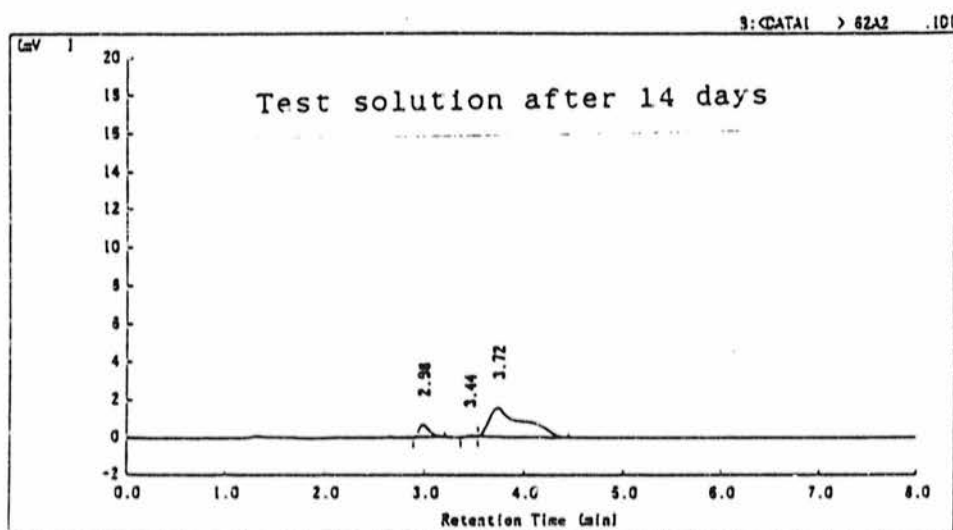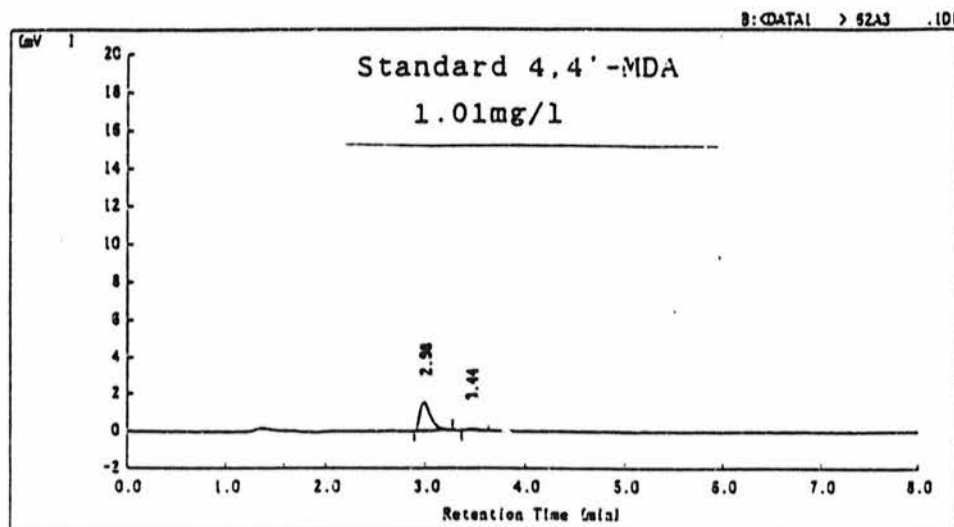water-polymeric MDI phases; 18.1 cm^2, Temperature; 25°C.

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Figure 33. Comparison of chromatograms of test solution after
14 days in static experiment with that of standard solution of
4,4'-MDA. Test conditions: polymeric MDI;5g, Interface area be-
tween water-polymeric MDI phases; 18.1 cm^2, Temperature; 25°C.
HPLC condition was the same as that of the analysis of MDA except
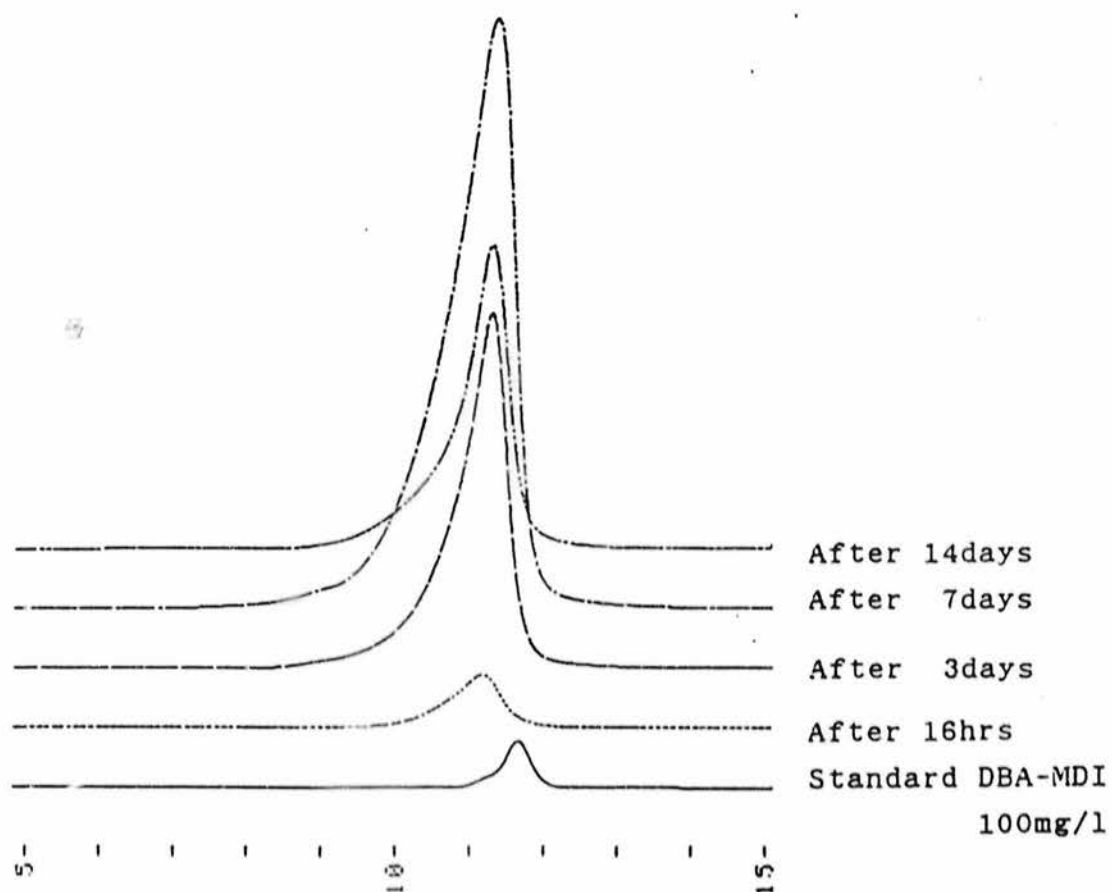detection wavelength (280nm).

Figure 34. Variation in GPC profile of the toluene-insoluble
reaction products soluble in LiCl-DMF in static experiment.
Test conditions: polymeric MDI;5g, Interface area between water-
polymeric MDI phases; 13.2 cm^2, Temperature; 25'C.

AMTEK CORP.

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